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INSTITUTE OF PETROLEUM.

An Ordinary General Meeting of the Institute of Petroleum was held at Manson House, 26, Portland Place, London, W.1, on Wednesday, October 8, 1947. Professor F. H. Garner, O.B.E. (Past-President), was in the Chair.

The minutes of the preceding Ordinary General Meeting, held on June 11, 1947, were read, confirmed and signed.

MR GEORGE SELL (Publications Secretary) read the names of candidates elected to membership of the Institute by the Council in accordance with the Bye-Laws at its meeting on October 8, 1947.

THE CHAIRMAN: The paper on "Metallurgical Methods for Combating Corrosion and Abrasion of the Petroleum Industry" was prepared by Mr B. B. Morton as the result of a request that data on this subject should be presented to some of the designers of petroleum equipment in Britain. It was, however, felt by him that the subject merited the wider audience represented by the Institute of Petroleum. Mr Morton is a specialist, so far as petroleum equipment is concerned, in the International Nickel Company, but unfortunately he is unable to be present. In his place Mr W. J. Burling-Smith, of the Mond Nickel Company, has very kindly consented to present the paper.

MR. W. J. BURLING-SMITH: I have to convey to you Mr Morton's very deep regret that unavoidable circumstances have prevented him making the journey to Britain to present this paper in person, as originally planned. I am quite sure we all share that regret.

Perhaps I should also explain, particularly for the benefit of those of you who have had an opportunity to read Mr Morton's paper, and in view of the wealth of information contained therein, that Mr Morton has prepared a summarized version, picking out the high spots of his paper; and it is that which I am to present to you.

A summary of the following paper was then read by Mr Burling-Smith.

METALLURGICAL METHODS FOR COMBATING CORROSION AND ABRASION IN THE PETROLEUM INDUSTRY.

By B. B. MORTON.*

THE action of corrosion and also of abrasion within the petroleum industry results in the wasting away of important material and the early retirement or destruction of equipment that is unprotected. The object of this paper is to review steps that have been taken within the petroleum industry of the United States to counteract such destruction and especially to outline recent metallurgical developments within the industry.

* Development and Research Division, The International Nickel Co. Inc., New York.

The war gave considerable impetus to the use of corrosion-resisting materials in refineries and has allowed an evaluation of much of them that might never have normally been employed on a scale large enough to permit a satisfactory study. The introduction of reagents, such as hydrofluoric acid and hydrochloric gas, called for rapid and intense study of new materials in service on a large scale. The need during the war to protect irreplaceable carbon steel vessels upset peace-time economics and justified the use of protective liners without consideration of their cost. All these factors tended to increase and to expand knowledge at a lively rate. Some of the information derived will be of present use; some will have to await application at the more leisurely pace of normal evolution.

The association of the writer with the Development and Research Division of The International Nickel Company Inc. has permitted an extensive viewing of the combat with corrosion. Not only does the D. and R. Division of this Company maintain close association with the groups of the petroleum industry charged with the study and combating of corrosion, but the corrosion test spools (Fig. 13) provided by this Division are ubiquitous in this industry as in nearly all industry of the United States confronted with corrosion problems.

The tremendous versatility of nickel, especially as an alloying element, has made collaboration almost inevitable. A large number of the most successful corrosion-resistant alloys are nickel-containing. It is felt that this information will prove gratifying, since nickel is largely produced in Canada—a member of the British Commonwealth.

The corrosion and mechanical problems of the petroleum industry are many and so varied that practically every metallic element has been employed in some form to aid in solving them. Some precious and semi-precious metals have been employed. Gold is the outstanding exception, and to the writer's knowledge has so far not been employed. This may be associated with its distinctive colour and to the lack of some desirable physical properties.

The petroleum industry is divided for the purpose of this paper into Production, Transportation, and Refining. Production is considered to deal with exploration, drilling, and pumping of the wells. Transportation deals with moving the crude, above the ground, and also the moving of finished products. Refining deals with treatment of the crude and fractions thereof to the end of producing a desired product. Marketing, a major division of the petroleum industry, is not considered in this paper.

In reviewing corrosion in the petroleum industry, one is prompted to seek broad generalities—usually without success. One does note a change in character in the corrosion encountered, especially in the refineries, depending upon the presence or absence of liquid water In the elevated temperature regions, where the water is present as a gas, if at all, the most useful materials are the stainless—*i.e.*, high chromium—alloys. Their composition, however, will depend upon the presence or absence of naphthenic or other organic acids. No such general classification of material can be made for the regions of temperature where liquid water is present to form acids or alkalies. The requirement does exist that a somewhat protective film must result from attack. This condition can be met by a variety of metals, depending upon the corrosive encountered, but, as

inferred, no one material so broadly serves this field as do the chromium alloys in the higher temperature fields.

Production.

Exploration.

Exploration for petroleum has developed into quite a science and embodies a large-size industry. The science makes demands upon unusual properties of metals as magnetostriction, high and low coefficients of expansion, and also special electrical and magnetic properties.

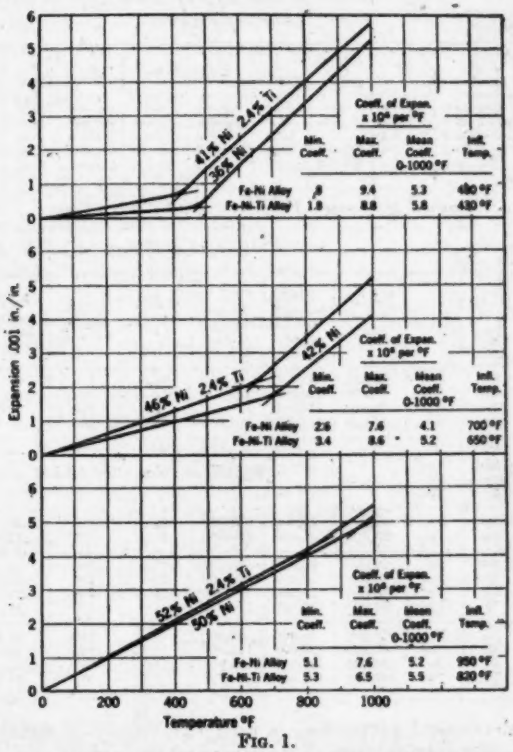


FIG. 1.

COMPARISON OF EXPANSION CHARACTERISTIC OF THREE TITANIUM-FREE FE–NI ALLOYS WITH THREE COMPARABLE NI–SPAN LO ALLOYS CONTAINING 2·4 PER CENT TI AND 0·06 PER CENT C.

The actual instruments are largely secrets of each major exploring group. In these instruments, and associated with them, nickel is used for its magnetostriction properties; K-Monel and Inconel for non-magnetic qualities combined with high strength, and other nickel alloys for low or high thermal expansion properties. In connexion with these last alloys, data on the Ni–Span group are provided in Table I, and Fig. 1.[1] The

Ni–Span Lo alloys are for use where low expansion properties are desired, combined with high strength. Ni–Span Hi alloy has a coefficient of expansion that is near the maximum known for ferrous base alloys (approximately 11 × 10^{-6} per deg F). Ni–Span C alloy is used where no change, or a controlled change in elastic characteristics with changes in temperature is desired.

Aluminium, due to its lightness in weight, to its resistance to corrosion,

TABLE I.

Range of Chemical Composition of Ni–Span Alloys.

Alloy.	Chemical composition, %.									
	Ni.	Ti.	Cr.	C (max).	Mn.	Si.	Al.	P (max).	S (max).	Fe.
Ni-Span Lo 42	40·5–42·5	2·2–2·6	—	0·06	0·3–0·6	0·3–0·8	0·4–0·8	0·04	0·04	bal.
Ni-Span Lo 45	44·5–46·5	2·2–2·6	—	0·06	0·3–0·6	0·3–0·8	0·4–0·8	0·04	0·04	bal.
Ni-Span Lo 52	51·0–53·0	2·2–2·6	—	0·06	0·3–0·6	0·3–0·8	0·4–0·8	0·04	0·04	bal.
Ni-Span Hi	28·0–30·0	2·2–2·6	8·0–9·0	0·06	0·3–0·6	0·3–0·8	0·4–0·8	0·04	0·04	bal.
Ni-Span C	41·0–43·0	2·2–2·6	5·1–5·7	0·06	0·3–0·6	0·3–0·8	0·4–0·8	0·04	0·04	bal.

Nominal Mechanical Properties of Ni–Span Alloys.

Alloy.	Condition.			Mechanical properties.						
	Solution treated.	Cold working, %.	Aging.	Proportional limit, p.s.i.	Yield strength 0·2% offset, p.s.i.	Tensile strength, p.s.i.	Elongation in 2 in., %.	Hardness Brinell, 3000 kg.	Tensile modulus of elasticity 10^{-6} p.s.i.	Torsional modulus of elasticity, 10^{-6} p.s.i.
Ni-Span Lo 42	Yes	No	No	20,000	40,000	90,000	32·0	140	21·0	—
	Yes	No	Yes	65,000	120,000	165,000	14·0	330	22·0	—
	Yes	50	No	70,000	115,000	130,000	3·0	240	22·5	—
	Yes	50	Yes	110,000	165,000	195,000	5·0	385	23·0	—
Ni-Span Lo 45	Yes	No	No	Slightly lower than Ni-Span Lo 42						
	Yes	No	Yes							
	Yes	50	No							
	Yes	50	Yes							
Ni-Span Lo 52	Yes	No	No	15,000	35,000	85,000	27·0	125	—	—
	Yes	No	Yes	55,000	95,000	120,000	17·0	305	22·0	—
Ni-Span Hi	Yes	No	No	20,000	35,000	80,000	30·0	140	—	—
	Yes	No	Yes	60,000	95,000	150,000	20·0	305	25·0	—
	Yes	50	No	60,000	120,000	140,000	4·0	250	24·5	—
	Yes	50	Yes	80,000	130,000	180,000	8·0	370	26·0	—
Ni-Span C	Yes	No	No	15,000	35,000	90,000	40·0	145	24·0	—
	Yes	No	Yes	65,000	115,000	180,000	18·0	345	26·5	10·0
	Yes	50	No	55,000	130,000	135,000	6·0	275	25·5	—
	Yes	50	Yes	105,000	180,000	200,000	7·0	395	27·0	10·0

and to its mechanical properties, is used extensively in connexion with exploration equipment as parts of carriages and equipment.

In regions where salt domes are indicative of the presence of petroleum, as in the Gulf Coast area of the United States, the seismograph is widely used in exploration. Trucks equipped with a magnificent array of instruments are stationed in locations surrounding a point where a miniature well is drilled in which an explosive is set off. The waves from the explosive are picked up and recorded in the trucks. From the data of time, intensity, and other factors, the presence or absence of an underground mass as a dome can be determined.

Electrical logging of wells also involves elaborate and expensive equip-

ment. A non-magnetic reel apparently is used which is constructed from K-Monel parts or from austenitic alloys of the nickel–chromium type.

The marsh buggy (Fig. 2) is used to transport equipment in the marshy coastal regions. The wheels are of Monel in the case of the vehicle shown. Rubber tyres are also used to give buoyancy to the wheels.

Drilling.

Drilling within the United States is done by two methods, namely, rotary (Fig. 3) and by cable tool. Cable-tool drilling is the older method and apparently is as old as recorded history. Its operation consists in raising and dropping a weight, the bit, and thereby pulverizing rock and soil. The crushed debris is mechanically removed by lowering a bailing device. The cable and other parts, such as "jars," "grief stem," and bit necks, are subjected to reversals of stresses, hence to fatigue failure. When failure occurs, the parts must be "fished" out. The fishing tools are models of ingenuity. They represent an unbelievable variation in size, shape, and functions. When the fishing tool has taken hold of the severed part, "up-jarring" is resorted to in order to loosen the part. The fishing tool itself is highly stressed and must resist a high order of tensile impact. 3 to 5 per cent nickel steels, also nickel–chromium steels, are used for this work. The bit is of high carbon steel. Here alloys have not been able to supplant this carbon steel. The jars are made of chromium–vanadium steel.

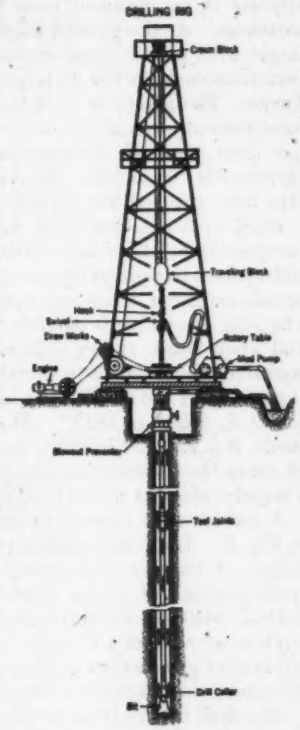


FIG. 3.
ROTARY DRILLING EQUIPMENT.

With the growth of the metallurgical arts, and the resulting improvement in steel qualities, the rotary method has largely displaced the cable tool for drilling. Cable-tool drilling is now largely confined to the northeastern part of the U.S.—Pennsylvania, Ohio, Michigan, etc. In other parts of the country—Texas, Oklahoma, California, etc.—use is made of rotary drilling. The basis for the demarcation of each type of drilling is not known, though many reasons are assigned.

In view of the more extensive use of rotary drilling in the United States, this paper will give it greater consideration.

The drilling operations mainly make demands upon the mechanical properties of steels and certain alloys. It is rather noteworthy that the rotary equipment in present use can go to considerable depths since holes deeper than 16,000 feet have been drilled with equipment corresponding to

what is considered standard from the standpoint of conforming to the specifications of the American Petroleum Institute [2] covering drilling equipment.

In the matter of drill-pipe, the high manganese carbon steel conforming in properties to Grade D of the A.P.I. Specification No. 5 appears to be quite satisfactory. Some investigation has been made of alloy drill-pipe, and a nickel–copper (approx. 0·17 C, 1·75 Ni, 1·0 Cu) composition of the trade name "Yoloy" [3] has been used with satisfaction in connexion with some of the deeper wells. The chief problem associated with drill-pipe appears to be abrasion from the mud and corrosion fatigue in certain locations. At the present time some of the drill-pipe has been lined on the inside with plastic compositions, and has been reported to give improved performance from the standpoint of resisting corrosion fatigue in western Texas. The plastic is soon scoured off by the mud, but even under this condition the overall life has been reported as increased. Some attention has been given to drill-pipe nickel plated on the inside and chromium plated over the nickel. No results from experience with this type of drill-pipe have reached the writer.

Hard-surfacing materials, such as the tungsten, boron, and chromium compositions, which form carbides of these elements when deposited, are widely used to protect the cutting edges of the bits. Stellite,[4] a chromium–cobalt–tungsten alloy, is widely used, especially for "fish-tail" bits. The rock bit, which is possibly the most interesting development in drilling and upon which rotary drilling must depend for its existence, represents considerable advances in metallurgy (Fig. 4). The bit, body, cutters, and support arms are usually of a nickel–molybdenum alloy steel corresponding to S.A.E. 4620 * or 4815.* The cutters are made from nickel–molybdenum steels, S.A.E. 4620 or 4815, case-hardened, and then hard-surfaced by use of one of the commercial hard-surfacing materials. Tungsten is apparently a popular element in the hard-facing material used for cutters.

A considerable tonnage of steel is consumed in the tool joints illustrated in Fig. 5. These tool joints are subjected to a variety of stresses of a high order. A number of materials have been used in their manufacture, the most popular of which have been X3140 (Ni–Cr), 4140 (Cr–Mo), and A.I.S.I. 8640 (Ni–Cr–Mo). Prior to the war there was a tendency to use a triple alloy steel of a composition approaching that of A.I.S.I. 4340. This triple alloy gave a very good account of itself in the field, and there is a trend to resume its composition for the more highly stressed tool joints.

The drill collars (Fig. 6) used to localize weight above the bit, and the "kellys" used to transmit the rotary motion of the table to the drill string are conventionally of steel corresponding to S.A.E. 4140, 3140, and 8640.

There has gradually grown up in the minds of those associated with the use of metals in petroleum drilling operations the feeling that the usually determined mechanical values as ultimate strength, yield point, elongation, and reduction of area of steel do not adequately predict the behaviour to be expected from parts, such as tool joints, drill collars, "kellys," etc., in service. Attention is now somewhat focused on impact values as being indicative in connexion with other properties. In other words, of two steels

* For compositions, see Table II.

TABLE II.

Composition of Steels Referred to in Text.

S.A.E. number.	Nominal chemical ranges.								A.I.S.I. number.	Type.
	C.	Mn.	P.	S.	Si.	Ni.	Cr.	Mo.		
1020	0·18/0·23	0·30/0·50	0·040	0·050	—	—	—	—	C1020	Carbon steel
1335	0·33/0·39	1·60/1·90	0·040	0·040	0·20/0·35	—	—	—	C1142	Manganese steel
2515	0·12/0·17	0·40/0·60	0·040	0·040	0·20/0·35	4·75/5·25	—	—	A2515	Nickel steel
(X3140)	0·38/0·43	0·70/0·90	0·040	0·040	0·20/0·35	1·10/1·40	0·70/0·90	—	A3141	Nickel chromium
4140	0·38/0·43	0·75/1·00	0·040	0·040	0·20/0·35	—	0·80/1·10	0·15/0·25	A4140	Chromium molybdenum
4340	0·38/0·43	0·60/0·80	0·040	0·040	0·20/0·35	1·65/2·00	0·70/0·90	0·20/0·30	A4340	Nickel chromium molybdenum
4615	0·13/0·18	0·45/0·65	0·040	0·040	0·20/0·35	1·65/2·00	—	0·20/0·30	A4615	Nickel molybdenum
4620	0·17/0·22	0·45/0·65	0·040	0·040	0·20/0·35	1·65/2·00	—	0·20/0·30	A4620	Nickel molybdenum
4815	0·13/0·18	0·40/0·60	0·040	0·040	0·20/0·35	3·25/3·75	—	0·20/0·30	A4815	Nickel molybdenum
A.I.S.I. 8640	0·38/0·43	0·75/1·00	0·040	0·040	0·20/0·35	0·40/0·70	0·40/0·60	0·15/0·25	A8640	Nickel chromium molybdenum

TABLE II—*continued.*

Composition of Stainless Steels.

Type number.	Chemical composition, %.							
	C.	Mn max.	Si max.	P max.	S max.	Cr.	Ni.	Other elements.
301	Over 0·08/0·20	2·00	1·00	0·040	0·030	16·00/18·00	6·00/8·00	—
302	Over 0·08/0·20	2·00	1·00	0·040	0·030	17·00/19·00	8·00/10·00	—
302B	Over 0·08/0·20	2·00	2·00/3·00	0·040	0·030	17·00/19·00	8·00/10·00	—
303	0·15 max	2·00	1·00	—	—	17·00/19·00	8·00/10·00	P, S, Se min 0·07, Zr, Mo max 0·60
304	0·08 max	2·00	1·00	0·040	0·030	18·00/20·00	8·00/11·00	—
305	0·12 max	2·00	1·00	0·040	0·030	17·00/19·00	10·00/13·00	—
308	0·08 max	2·00	1·00	0·040	0·030	19·00/21·00	10·00/12·00	—
309	0·20 max	2·00	1·00	0·040	0·030	22·00/24·00	12·00/15·00	—
310	0·25 max	2·00	1·50	0·040	0·030	24·00/26·00	19·00/22·00	—
314	0·25 max	2·00	1·5/3·0	0·040	0·030	23·00/26·00	19·00/22·00	—
316	0·10 max	2·00	1·00	0·040	0·030	16·00/18·00	10·00/14·00	Mo 2·00/3·00
317	0·10 max	2·00	1·00	0·040	0·030	18·00/20·00	11·00/14·00	Mo 3·00/4·00
321	0·08 max	2·00	1·00	0·040	0·030	17·00/19·00	8·00/11·00	Ti 5 × C min
347	0·08 max	2·00	1·00	0·040	0·030	17·00/19·00	9·00/12·00	Cb 10 × C min
403	0·15 max	1·00	0·50	0·040	0·030	11·50/13·00	—	Turbine quality
405	0·08 max	1·00	1·00	0·040	0·030	11·50/13·50	—	Al 0·10/0·30
406	0·15 max	1·00	1·00	0·040	0·030	12·00/14·00	—	Al 3·50/4·50
410	0·15 max	1·00	1·00	0·040	0·030	11·50/13·50	—	—
414	0·15 max	1·00	1·00	0·040	0·030	11·50/13·50	1·25/2·50	—
416	0·15 max	1·25	1·00	—	—	12·00/14·00	—	P, S, Se min 0·07, Zr, Mo max 0·60
420	Over 0·15	1·00	1·00	0·040	0·030	12·00/14·00	—	—
430	0·12 max	1·00	1·00	0·040	0·000	14·00/18·00	—	—
430F	0·12 max	1·25	1·00	—	—	14·00/18·00	—	P, S, Se min 0·07, Zr, Mo max 0·60
431	0·20 max	1·00	1·00	0·040	0·030	15·00/17·00	1·25/2·50	—
440A	0·60/0·75	1·00	1·00	0·040	0·030	16·00/18·00	—	Mo 0·75 max
440B	0·75/0·95	1·00	1·00	0·040	0·030	16·00/18·00	—	Mo 0·75 max
440C	0·95/1·20	1·00	1·00	0·040	0·030	16·00/18·00	—	Mo 0·75 max
446	0·35 max	1·50	1·00	0·040	0·030	23·00/27·00	—	N_2 0·25 max
501	Over 0·10	1·00	1·00	0·040	0·030	4·00/6·00	—	—
502	0·10 max	1·00	1·00	0·040	0·030	4·00/6·00	—	—

A.I.S.I. April 16. 1947.

A.I.S.I. April 16, 1947.

with the same mechanical properties other than impact values, the one with the higher impact value would be expected to give better performance under the complex stresses of drilling. The nickel–chromium–molybdenum (A.I.S.I. 4340) or nickel–chromium–vanadium alloy steels are considered to be outstanding in their ability to combine the properties of strength and impact.

Along this line a most interesting matter came to light involving guns used in perforating casing of oil wells, to permit drawing oil from a higher formation. For the benefit of those not acquainted with the practice of perforating casing, it will be explained that a bar of steel is drilled and "guns" are screwed into the holes. These guns carry charges of explosives and a bullet. The assembly is lowered to the desired point and the charge is set off by a current. The detonating charge drives the bullet through the casing (possibly two or three layers) and through the concrete

TABLE III.

Approximate Compositions of some High Nickel Alloys.

Material.	Nickel, %	Copper, %	Iron, %	Chromium, %	Molybdenum, %	Aluminium, %	Silicon, %	Manganese, %	Tungsten, %	Carbon, %
Nickel	99·4 ‡	0·1	0·15	—	—	—	0·05	0·2	—	0·1
*Monel	67·0	30·0	1·4	—	—	—	0·1	1·0	—	0·15
*H Monel †	65·0	29·5	1·5	—	—	—	3·0	0·9	—	0·1
*S Monel †	63·0	30·0	2·0	—	—	—	4·0	0·9	—	0·1
*K Monel	66·0	29·0	0·9	—	—	2·75	0·25	0·4	—	0·15
*Inconel	79·5	0·2	6·5	13·0	—	—	0·25	0·25	—	0·08
*Hastelloy A	53·0	—	22·0	—	22·0	—	1·0	2·0	—	—
*Hastelloy B	60·0	—	6·0	—	32·0	—	1·0	1·0	—	—
*Hastelloy C †	51·0	—	6·0	17·0	19·0	—	1·0	1·0	5·0	—
*Hastelloy D †	85·0	3·0	—	—	—	1·0	10·0	1·0	—	—
*Illium G †	60·0	4·0	6·0	21·0	6·0	—	1·0	1·0	1·0	—
*Illium R	60·0	3·0	8·0	21·0	5·0	—	1·0	1·0	1·0	—
LaBour †	53·0	5·0	8·0	23·0	4·0	—	4·0	0·5	2·0	—
*Duramet T	22·0	1·0	bal.	19·0	3·5	—	—	—	—	0·07
*Worthite	24·0	1·7	bal.	20·0	3·0	—	3·3	0·6	—	0·07

* Registered trade name. † Including cobalt. ‡ Only as castings.

between the casings. The force of the explosion can be imagined. The problem of a suitable material for the gun arose, and a number of alloy steels were tested. Since all of the steels could develop the same order of hardness (50–52 Rc, hence the same ultimate strength), service records had to be relied upon for selection of a steel. Final selection fell upon the nickel–chromium steel of the so-called Krupp analysis, or S.A.E. 3335.* Also, a gun-type alloy steel containing 2 to 3 per cent nickel with 1·5 per cent chromium with molybdenum and vanadium present has given excellent service when heat treated to 52 Rockwell C hardness. The behaviour of these guns indicated that the presence of more than 2·5 per cent nickel in a steel for this service seems necessary with other elements to allow complete hardening throughout the walls, which are $\frac{3}{4}$ in to 1 in thick. The benefit from the high nickel compositions is assumed to be a higher order of impact value than that obtained from other steels of the same hardness. The matter is still being studied.

The requirements associated with directional drilling have necessitated a non-magnetic material for drill collars and, after some extensive tests,

* S.A.E. 3335. Not a standard composition—a 3·25 to 3·75 per cent Ni; 1·40 to 1·75 chromium; with 0·30 to 0·40 carbon.

K-Monel (see Table III) has been adopted and is widely used (Fig. 7). This alloy is furnished to a specification of :

TABLE IV.

Specification Values for K-Monel Non-Magnetic Drill Collars.[8]

Ultimate strength	120,000 p.s.i. (min)
Yield strength	75,000 p.s.i. „
Elongation	20% „
Permeability	1·02 (air taken as 1·00) (max)

The greater density of K-Monel gives it 10 per cent greater weight for a given volume. This is considered as advantageous for these K-Monel collars since it is an aid in the effort to concentrate weight above the bit.

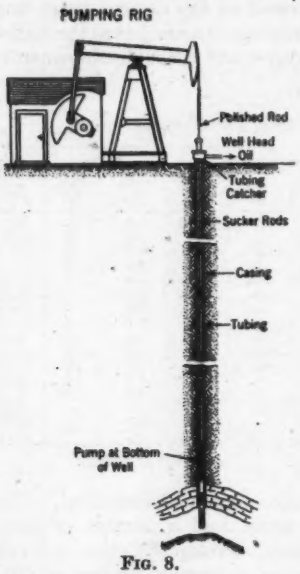


FIG. 8.
A PETROLEUM PUMPING RIG.

The slush pumps, used in rotary drilling to force mud down the drill-pipe so that it can bring the chips and cuttings to the surface outside of the drill-pipe, offer problems in the matter of resisting abrasion. Rubber is the most useful material so far as resisting the abrasion of the mud is concerned, and will be found an important part of pump valves and in other locations where it can be utilized. The liners of these pumps are often made up from S.A.E. 4620, carburized on the inside, or from induction-hardened carbon-manganese steel. They are also formed by lining the inner surface with an abrasion-resisting material, principally a nickel–boron form of cast iron. This material melts at a temperature below the melting point of the steel liner, and, as a result, it can be spun by revolving the liner while the protective material is molten. Rods of carburized steel, such as S.A.E. 4620, 4815, and other compositions, appear to give satisfactory service if care is taken to prevent the retention of austenite.

The greater part of the equipment used in connexion with drilling is highly stressed, as has been pointed out. However, there are a large number of excellent steels which can readily withstand the stresses of operation, for, as mentioned previously, this point has been established by the drilling of very deep wells with the use of steels now commonly used.

Pumping.

Petroleum is raised to the surface along with its attending salt water by one of three means, namely : (1) flowing under pressure of the reservoir ; (2) by mechanical pumping (Fig. 8); and (3) by gas lifting (Fig. 9). Mechanical pumping is decidedly the most popular method of raising petroleum from reservoirs where the pressure is no longer sufficient to cause

it to flow to the surface. In mechanical pumping, a reciprocating pump is installed at the bottom of the tubing and the power at the surface of the earth is transmitted down to the pump by coupled rods, referred to in the industry as " sucker-rods."

(a) *Sucker-Rods.*

The selection of sucker-rod materials has engaged considerable attention since these rods represent an appreciable item of expense in the matter of pumping petroleum. The composition of the steel from which the sucker-rods are formed changes with the presence or absence of corrosion as shown in Table V. The chief requirements for sucker-rods are high yield point, and in corrosive areas a high retention under corrosion of the endurance limit determined in the atmosphere. As a result of considerable study and practical experience, the nickel-containing alloy steels are the most widely used under corrosive pumping conditions, since they appear to retain to a higher degree their endurance limit as determined in air (Table VI). The tendency, in time, has been to increase the content of the nickel from about 1½ per cent to the order of 3½ per cent as the more corrosive wells are placed " on the pump."

In summary of Table V, it will be seen that carbon–manganese steels are used to resist stress without corrosion, and nickel steels to resist both.

The benefit of nickel is being further explored by the recent installation of a string of rods from an 8½ per cent nickel steel containing about 0·12 per cent carbon. The mechanical values obtained from this steel are listed in Table VII.

The most resistant rods to extremely corrosive conditions so far used are rods that have been nickel plated with about 0·006 in of nickel. These rods have given an excellent account of themselves in fields very corrosive owing to the presence of hydrogen sulphide, such as some West Texas wells, and also in wells that have corrosive brine in which sulphur is missing. The nickel plating is quite resistant to the corrosives, and the rods will be protected so long as the nickel plating is not mechanically destroyed, as it can be by striking the walls of the tubing. The absence of undercutting of abraded rod casts some doubt upon the action of marked galvanic corrosion in oil wells where oxygen is missing.

K-Monel, by virtue of its high mechanical strength (Table VIII), has been successfully used as sucker-rods in very corrosive fields (Fig. 10), and it apparently is the most resistant material so far discovered, possessing the order of mechanical properties given in Table VIII. Experience shows K-Monel to be as resistant to corrosion as the nickel plating referred to above, and the rods of K-Monel are immune from destruction as the result of striking the tube walls.

The present interest in the United States is towards rods suitable for pumping very deep wells. It is anticipated that wells of 9000 feet and deeper will be " on the pump " in the near future, and the problem of the sucker-rods for such wells is being studied. At the present moment attention is directed to both K-Monel and to the 8·5 per cent nickel steel as possible materials for the rods at the upper end of the well. Undoubtedly tapered strings will be used and the composition will be set by the corrosive conditions existing when the time comes to pump the very deep wells.

TABLE V.

Representative Sucker-Rod Alloys for Varying Conditions of Stress and Corrosion.

Condition.	A.		B.	
	Type.	Mechanical properties.	Type.	Mechanical properties.
Light pumping—No corrosion	C–1038 modified (C steel)	Y.P. 55/65,000 p.s.i. El 8 inches 18/24% Izod 50/60 ft.-lb.	S.A.E. 1035/45	Y.P. 50,000 p.s.i. (min)
Heavy pumping – no corrosion	C–1036 modified (C–Mn)	Y.P. 65/75,000 p.s.i. El 8 inches 18/23% Izod 60/90 ft.-lb.	A1335 (C–Mn)	Y.P. 70,000 p.s.i. (min) El Izod
Light pumping—moderate corrosion	A4621 (Ni–Mo)	Y.P. 65/75,000 p.s.i. El 8 inches 20/25% Izod 90/105 ft.-lb.	A4615 (Ni–Mo)	Y.P. 65,000 p.s.i. (min)
Heavy pumping –Moderate corrosion	A4621	Y.P. 65/75,000 p.s.i. El 8 inches 20/25% Izod 90/105 ft.-lb.	A4615–Nickel plated * (Ni–Mo)	Y.P. 65,000 p.s.i. (min)
Light pumping—vigorous corrosion	A4815 (Ni–Mo) *Or* K–Monel (heat treat.) *	Y.P. 75/85,000 p.s.i. El 8 inches 20/25% Izod 90/110 ft.-lb. Y. strength—100/110,000 p.s.i. El 8 inches 20·0% min	A4615–Nickel plated *	Y.P. 65,000 p.s.i. (min)
Heavy pumping—vigorous corrosion	A4815 *Or* K–Monel (heat treat.) *	Y.P. 75/85,000 p.s.i. As above	A3310 (Ni–Cr) A1335–Nickel plated †	Y.P. 70/90,000 p.s.i. (min)

Condition.	C.		D.	
	Type.	Mechanical properties.	Type.	Mechanical properties.
Light pumping—no corrosion	C–1043 (C–Mn)	Y.P. 50,000 p.s.i. (min) El Izod 50 ft.-lb. (min)	C 0·28/0·38 Mn 1·20/1·50 Not heat treated	Y.P. 50,000 p.s.i. (min) El (4D) 25% min Izod 15 ft.-lb. (min)
Heavy pumping—no corrosion	C–1036 (C–Mn)	Y.P. 60,000 p.s.i. (min) El Izod 60 ft.-lb. (min)	S.A.E. 4140 Quench and temp.	Y.P. 95,000 p.s.i. (min) El (4D) 22% Izod 85 ft.-lb. (min)
	A1335 (C–Mn)	Y.P. 70,000 p.s.i. Izod 55 ft.-lb.	C 0·28/0·38 Mn 0·80/1·10 Quench and temp.	Y.P. 85,000 p.s.i. (max)
Light pumping—moderate corrosion	A4621 (Ni–Mo)	Y.P. 65,000 p.s.i. (min) El Izod 85 ft.-lb.	C 0·30/0·40 Ni 1·25/1·75 Cr 0·60/0·90 Norm. and temp.	Y.P. 60,000 p.s.i. (min) El (4D) 25% Izod 65 ft.-lb.
Heavy pumping—moderate corrosion	A4621	Y.P. 65,000 p.s.i. (min) El Izod 85 ft.-lb.	C 0·10/0·20 Ni 1·25/1·75 Mo 0·15/0·20 Quench and temp.	Y.P. 70,000 p.s.i. (min) El (4D) 25% Izod 90 ft.-lb.
Light pumping—vigorous corrosion	A4817 (3·5 Ni–Mo)	Y.P. 70,000 p.s.i. (min) El Izod 95 ft.-lb.	C 0·05 max Ni 3·25/3·75 Mo 0·15/0·30 Quench and temp.	Y.P. 65,000 p.s.i. (min) El (4D) 25% Izod 90 ft.-lb.
Heavy pumping—vigorous corrosion	A4817	Y.P. 70,000 p.s.i. (min) El Izod 95 ft.-lb.		

* Precipitation hardened at 1080° F for 4 hours or more.
† About 0·006 inch nickel plate used on rods.
Note.—Carbon steel normalised. Alloy steel normalised and temp.

TABLE V—*continued.*

Representative Compositions of Sucker-Rod Materials of Table.

	C.	Mn.	P.	S.	Si.
C–1038	0·35/0·42	0·60/0·90	0·04 max	0·05 max	0·15/0·30
C–1036	0·32/0·39	1·20/1·50	0·04 max	0·05 max	0·15/0·30
A–4621	0·18/0·23	0·70/0·90	0·04 max	0·04 max	0·20/0·35
A–4815	0·13/0·18	0·40/0·60	0·03 max	0·03 max	0·20/0·35
K-Monel	0·15	0·40	—	0·005 max	1·00
S.A.E. 1035/45	0·32/0·38	0·60/0·90	0·04 max	0·050 max	—
A–1335	0·33/0·38	1·60/1·90	0·040 max	0·040 max	0·20/0·35
A–4615	0·13/0·18	0·45/0·65	0·040 max	0·040 max	0·20/0·35
A–3310	0·08/0·13	0·45/0·60	0·025 max	0·025 max	0·20/0·35
C–1043	0·40/0·47	0·70/1·00	0·040 max	0·050 max	—
A–4817	0·15/0·20	0·40/0·60	0·040 max	0·040 max	0·20/0·35

	Ni.	Mo.	Cr.	Cu.	Al.
C–1038	—	—	—	—	—
C–1036	—	—	—	—	—
A–4621	1·65/2·00	0·20/0·30	—	—	—
A–4815	3·25/3·75	0·20/0·30	—	—	—
K-Monel	66·00	—	—	29·00	2·75
S.A.E. 1035/45	—	—	—	—	—
A–1335	—	—	—	—	—
A4615	1·65/2·00	0·20/0·30	—	—	—
A–3310	3·25/3·75	—	1·40/1·75	—	—
C–1043	—	—	—	—	—
A–4817	3·25/3·75	0·20/0·30	—	—	—

TABLE VI.

Endurance Limit of Five Types of Sucker-Rod Steels.

	Air, p.s.i.	Salt water, p.s.i.	Hydrogen sulphide, p.s.i.
Carbon steel : C 0·37/0·44 Mn 0·70/1·00	51,600	19,900	10,900
Carbon–manganese steel : C 0·30/0·37 Mn 1·20/1·50	52,600	21,900	16,100
Nickel–molybdenum steel : C 0·18/0·23 Mn 0·70/0·90 Ni 1·65/2·00 Mo 0·20/0·30	52,500	33,100	22,500
High nickel–molybdenum steel : C 0·13/0·18 Ni 3·25/3·75 Mo 0·20/0·30	60,000	37,500	24,500
High nickel–copper alloy : C 0·07/0·13 Mn 0·20/0·50 Ni 3·00/3·50 Cu 1·45/1·65	64,000	36,000	24,000

Compilation of published data, notably : S. M. Jones Co., W. C. Norris Co., and Emsco Derrick and Equipment Co.

TABLE VII.

Some Mechanical Values Obtained from a 8½% Nickel Steel Proposed for Sucker-Rod Service.

Ultimate tensile strength, p.s.i.	115,000
Yield strength, p.s.i.	104,000
Elongation in 2 inches, %	26
Reduction in area, %	64
Endurance limit (air), p.s.i.	72,000
Ratio, endurance limit/ultimate tensile strength, %	62

Note.—Double normalized and drawn at 1050° F.

TABLE VIII.

Mechanical Properties of K-Monel Sucker-Rods (Hot-Rolled and Aged Material).

Ultimate tensile strength, p.s.i.	152,000
Yield strength, p.s.i.	103,000
Elongation, in 8 inches, %	25·8
Reduction in area, %	43·5

(Courtesy of W. C. Norris, Manufacturers, Tulsa, Okla.)

Endurance limit, air, p.s.i.	44,000–58,000 *

* See discussion, p. 58.

(b) *Oil-Well Pumps.*

The pumps in oil wells are exposed to all the corrosives that attack the sucker-rods, and the tendency is towards corrosion-resistant materials. Fig. 11 represents a pump manufactured by Harbison Fisher Company, Fort Worth, Texas, and represents a most intelligent application of the various grades of Monel. Here the corrosion resistance of Monel is applied as well as the gall-resisting characteristics of the silicon (S-Monel) variety, and also the hardness obtainable from the K-Monel type. It is expected that this pump will be free from corrosion in even the most corrosive wells of West Texas.

(c) *Gas-Lift Equipment.*

Gas-lift equipment is subject to corrosion, to wire drawing, and to some abrasion. Fig. 9 shows a gas-lift valve widely used, and it will be noted that the entire valve is of Monel of various grades. The various parts were from time to time made of different materials, and this particular valve represents an evolution dictated by the corrosion encountered over a very long period of time.

(d) *Ball Valves.*

The matter of valves for oil-well pumps has received considerable attention. The material should be hard and corrosion resistant. Heat-treated K-Monel (Fig. 12) has been outstandingly successful when used in corrosive wells of medium depth (2000 to 3500 feet). Below this depth the K-Monel lacks sufficient hardness to function satisfactorily. Heat-treated stainless steel (approximately 1·0 per cent carbon, 14 to 18 per cent chromium) possesses the hardness, but in corrosive wells is attacked and balls have ruptured as a result of the internal stresses acting on the corroded area.

A ball and seat of Stellite (Cr–Co–W alloy) has been reported as most

satisfactory from the standpoint of hardness and corrosion resistance in deep wells.

Some " precision cast " S-Monel drops and seats are on trial, and results are awaited with interest. The drop is a light-weight part to replace the ball.

(e) *Polished Rods.*

Polished rods come in for considerable wear, and are subject to corrosion in a number of wells. This is the rod that passes through the stuffing-box at the well-head which serves to connect the sucker-rods with the motive power at the surface (see Fig. 8). In the absence of marked corrosion, these rods are usually made from steel, such as carbon steel or the low alloy steels of the carbon–manganese type. Where corrosion is felt, the composition usually follows the composition of the sucker-rods and is often a nickel–molybdenum alloy steel such as A4615. For very corrosive conditions, Monel is a popular polished rod and has given an excellent account of itself, in very trying service. Brass and bronze are also extensively used to resist corrosion as a solid polished rod and as a tubing over steel rods. The higher mechanical properties obtainable from the heat-treatable form of Monel, K-Monel, has directed quite a lot of attention to this alloy, and it is being considered for use where very heavy pumping is anticipated in a corrosive location.

It will be noted in the foregoing that a great deal of space is devoted to Monel of various compositions. This is because the environment is favourable to this alloy. The brines, weak acids, and cold hydrogen sulphide all tend to build up a film resistant to continued corrosion. In the case of the plated sucker-rods, the 0·006 inch of nickel had not been penetrated during 6 to 8 years. Bronzes share with Monel a high order of corrosion resistance in wells, and use is made of bronze parts, sucker-rods, etc. Bronze lacks the hardness and strength of Monel, especially K-Monel, hence its use is limited.

The absence of oxygen, or a film-forming compound, has limited the use of stainless steel in production from very corrosive wells. Sulphur attack is not protective to stainless at the low temperatures involved. Much stainless of the 18–8 type is used in moderately corrosive wells.

Transportation.

General.

Petroleum and its products are transported by means of ocean-going tankers, pipelines, railway-tank cars, and tank-carrying trucks. The greatest volume in the United States is moved by means of the tankers and by the pipelines, with economics favouring the tankers for long hauls.

Tankers.

The ocean-going tankers represent a sizeable investment which is continuously deteriorated by the corrosion encountered, principally on the inside. A great deal of study has gone into the possible protection of

the tanks, but to date no satisfactory and at the same time economical method has been evolved. The corrosion is complicated by the fact that the light ends tend to remove paint or plastic covering, and there is danger of contamination as these protections are removed.

The most severe corrosion is in those tanks in which gasoline and light products are transported. This is due to the fact that these products leach the walls and so lay them bare to the corrosion that will occur when the tank is emptied, or when ballast is carried. The system of washing down the tanks with hot salt water is considered as a contributing factor to the

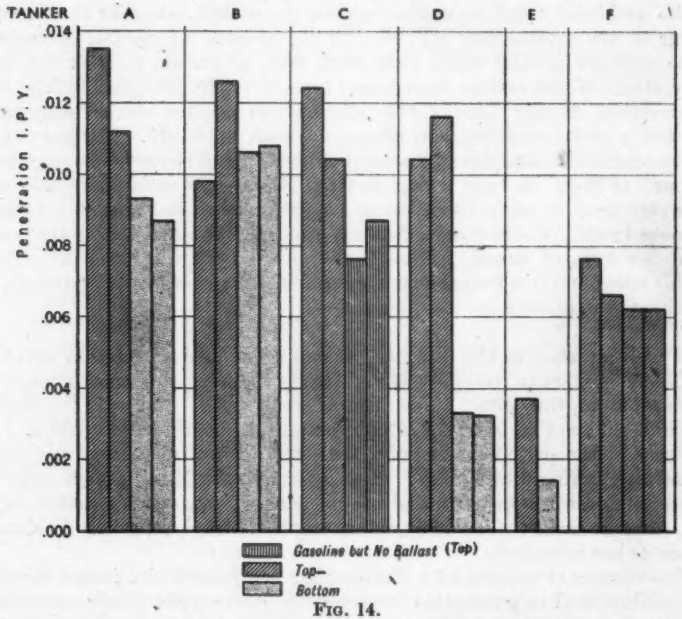


FIG. 14.

STUDY OF TANKER STEEL IN VARIOUS LOCATIONS AND SERVICES.

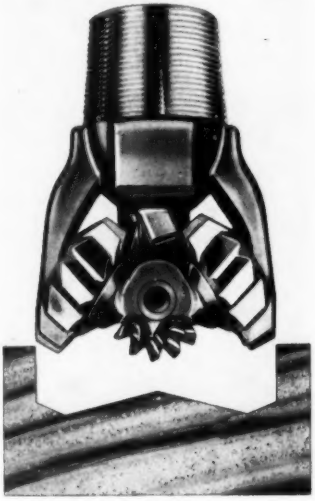
corrosion. The ballasting of the tankers by taking on a salt-water cargo also contributes appreciably to the corrosion.

Some time ago the Development and Research Division of the International Nickel Company, in co-operation with several groups in the oil companies, began a series of tests to ascertain if an alloy steel could be found that would increase the life of the tankers without uneconomically increasing the cost. As the first step in this investigation, sample test spools, as shown in Fig. 13, were installed in the top and bottom of cargo tanks. Some results obtained from tanker steel in various locations are illustrated by Fig. 14,[6] which is representative of the results obtained. Corrosion is most severe at the top, as has been generally considered. Alternating cargoes of gasoline and sea-water appeared to be more corrosive than gasoline alone. This combination has long been suspect. The effects of gasoline cargoes compared with crude cargoes were also noted. The cor-

[*Courtesy Ironcraft Inc.*

FIG. 2.

"MARSH BUGGY" USED TO TRAVERSE SWAMPY REGIONS IN CONNEXION WITH PETROLEUM EXPLORATION.



[*Courtesy Security Engineering Co.*

FIG. 4.

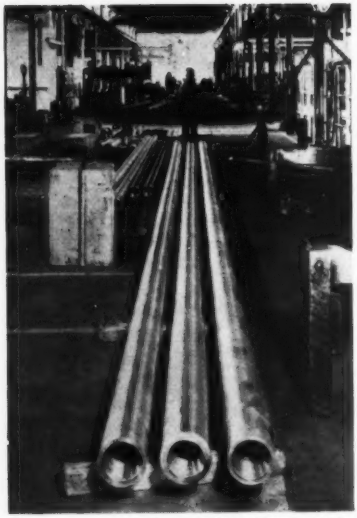
ROCK BIT.

[*Courtesy Reed Roller Bit Co.*

FIG. 5.

A STANDARD A.P.I. TOOL JOINT (S.A.E. 3140 STEEL).

[*To face p.* 16.



[*Courtesy Baash-Ross Tool Co.*

FIG. 6.

NICKEL–CHROMIUM STEEL (S.A.E. 3140) IS USED FOR THESE 55-FT DRILL COLLARS.

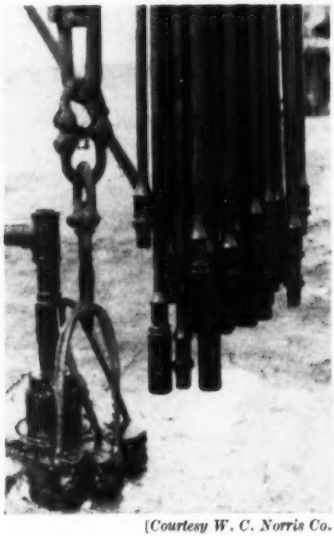
FIG. 7.

K-MONEL DRILL COLLAR (NON-MAGNETIC) USED IN OIL-WELL SURVEYING.

[*Courtesy Merla Tool Co.*

FIG. 9.

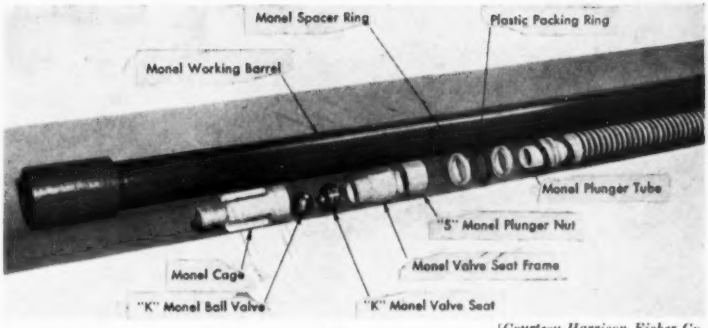
A GAS LIFT VALVE ENTIRELY OF MONEL.



[*Courtesy W. C. Norris Co.*

FIG. 10.

K-MONEL SUCKER RODS AND COUPLINGS AFTER ABOUT FOUR YEARS SERVICE IN WEST TEXAS.



[*Courtesy Harrison Fisher Co.*

FIG. 11.

OIL WELL PUMP DESIGNED TO RESIST WEST TEXAS CRUDE.

FIG. 12.

K-MONEL BALL AND SEAT VALVE.

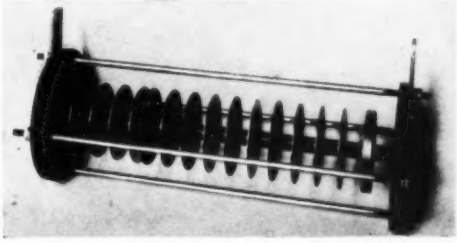


FIG. 13.

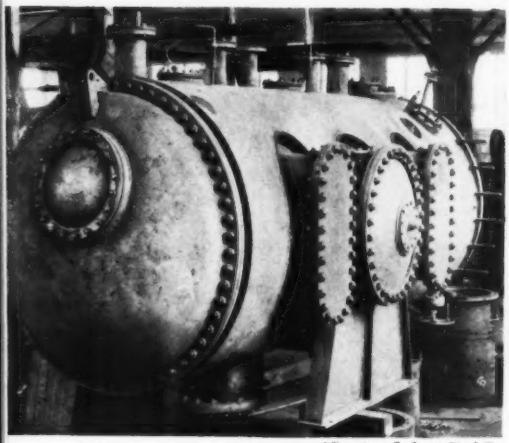
CORROSION TEST SPOOL PROVIDED BY DEVELOPMENT AND RESEARCH DIVISION OF THE INTERNATIONAL NICKEL CO.

FIG. 15.

NI RESIST CARGO PUMPS.

FIG. 16.

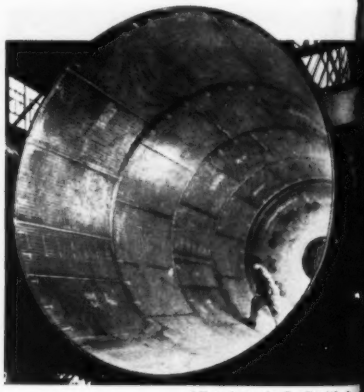
TEST OF VESSELS AT — 310° F. THE CARBON STEEL VESSEL (*left*) WAS CRACKED BY A HAMMER BLOW AND FAILED. THE $8\frac{1}{2}$ PER CENT NICKEL STEEL VESSEL (*right*) WITHSTOOD BLOWS FROM A 6-LB HAMMER AND THEN A 16-LB SLEDGE. NOTE THE INDENTATIONS.



[*Courtesy Lukens Steel Co.*

FIG. 18.

$3\frac{1}{2}$% NI STEEL VESSEL FOR USE AT — 160° F.



[*Courtesy A. O. Smith Co*

FIG. 19.

SMITH-LINED BUBBLE TOWER WITH 18–8 ON BOTTOM SECTION, MONEL OVER TOP DOME.

[*Courtesy Lukens Steel Co.*

FIG. 21.

0 PER CENT NICKEL CLAD STEEL PLATE, 152 IN. × 151 IN. × $\frac{3}{4}$ IN.

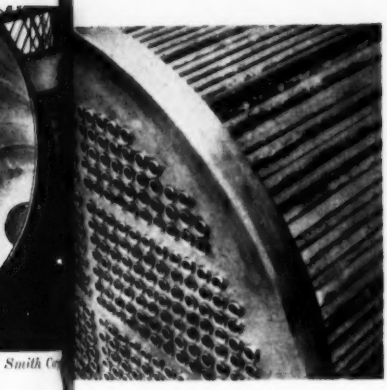
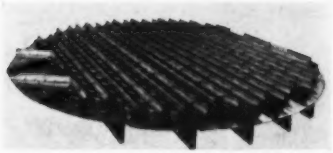


FIG. 21A.

ONEL CLAD TUBE SHEET. ORIGINAL PLATE 96 IN. × 72 IN. × $1\frac{1}{2}$ IN. WITH $\frac{1}{4}$ IN. MONEL. MONEL USED TO RESIST SALT WATER USED AS COOLANT, STEEL BACKING TO PERMIT NUMEROUS RE-ROLLINGS OF TUBES INTO SHEET.



[*Courtesy Fritz Glitsch & Co.*

FIG. 20.

CORROSION RESISTANT FABRICATED CAPS AND TRAYS.

[*Courtesy A. O. Smith Corpn.*

FIG. 22.

A. O. SMITH METHOD FOR APPLYING CORROSION RESISTANT LININGS TO STEEL PLATE.

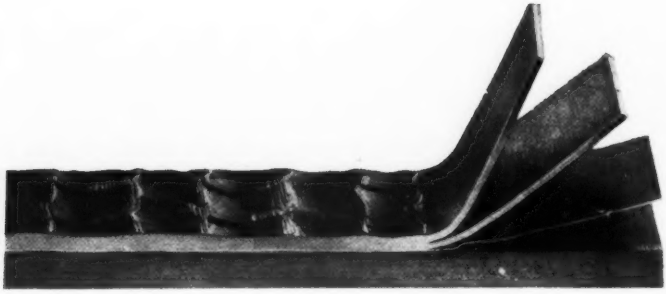


FIG. 23.

BABCOCK & WILCOX METHOD FOR CLADDING STEEL.

FIG. 23A.

SEGMENTS OF LARGE VESSELS FOR SERVICE IN THE FAR EAST PROTECTED AGAINST CORROSION BY THE B. & W. CLADDING METHOD.

FIG. 24.

STRIP LINING AN EXISTING VESSEL WITH CORROSION RESISTANT MATERIAL.

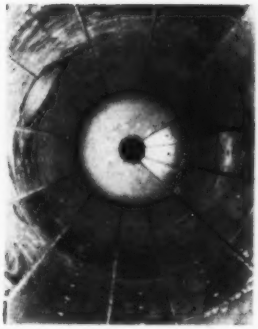
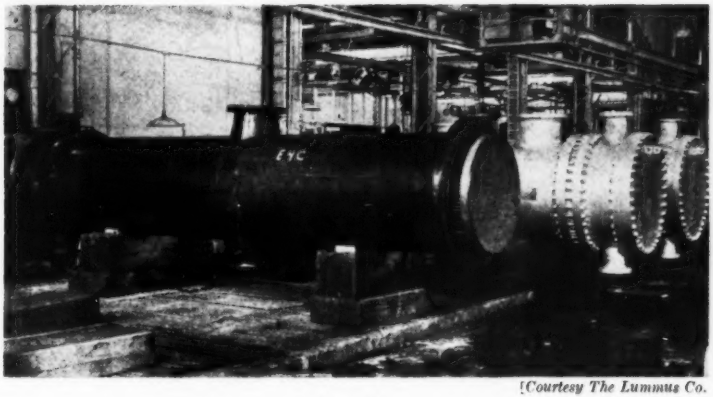


FIG. 25.

METHOD OF INSTALLING MONEL LINING IN EXISTING VESSELS.



[Courtesy The Lummus Co.

FIG. 26.

STEEL HEAT EXCHANGER SHELLS LINED WITH $\frac{5}{64}$ IN MONEL SHEET. THESE OPERATE AT 450° F WITH GASOLINE VAPOURS ON THE SHELL SIDE.

[*Courtesy Griscom–Russell Co.*

FIG. 27.

HEAT EXCHANGER CONSTRUCTED COMPLETELY OF MONEL FOR SERVICE IN A GULF COAST REFINERY. SEAMLESS TUBES ARE $\frac{3}{4}$ IN WITH $\frac{1}{16}$ IN WALL.

[*Courtesy Foster Wheeler Corpn.*

FIG. 31.

INCONEL HEAT EXCHANGERS FOR HIGH TEMPERATURE SERVICE.

rosion is least in "black oil" service. From a general study of many steels, the most resistant, from the standpoint of corrosion, was the 5 per cent nickel steel (S.A.E. 2515). This steel was considered to be too difficult to work and too expensive for practical application.

As a result of the study of the small specimens, a thought occurred that possibly the more vigorously attacked parts of the tank, usually the roof and possibly the bottom, could be made of some steel slightly noble to the tanker steel ordinarily used. By applying a more noble steel to the roof and bottom, the attack during the period that ballast was being carried would be directed against the carbon steel bulkheads and the sides which normally do not deteriorate at the rate of the top and bottom. This method of galvanic protection, while somewhat bizarre, attracted some attention, with the result that very elaborate installations of samples were made in the top, on the forward bulkhead, and on the bottom of a tank of an ocean-going tanker. About 2 tons of metal were involved and the specimens were insulated from the ship. The object of the test was to ascertain what galvanic protection could be expected and also the manner in which this would vary with the changes in relative areas of the noble and less noble material. Unfortunately, by the time these specimens were ready to be removed, the tanker was lost as an act of war.

Prior to this some thought had been given to installing rivets of a material slightly more noble than tanker steel in order to protect the rivet heads on the sea side at a slight expense of increased corrosion of the surrounding tanker steel. A number of rivets were installed and to date have been reported upon favourably. However, interest in riveting has almost entirely disappeared. The test rivets were of a steel containing about 1 to 1¼ per cent nickel, 0·10 to 0·20 carbon, designated as S.A.E. 2115.* The material has been accepted by the American Bureau of Shipping and Lloyds Register as a rivet material as a preliminary step to having test rivets installed.

The problem of tanker corrosion remains, and work is about to be undertaken again by exploration of the various materials under conditions encountered in the cargo tanks. At the present time several nickel-plated specimens have shown unusual resistance to attack in the top of the tankers, and a study along the lines of the use of plating may get under way by installing some deck plate, nickel plated on the bottom face. The nobility of the plating compared with the other parts of the structure will have to be considered with care.

Handling of tanker cargoes introduces the problem of corrosion. Fig. 15 shows some general utility cargo pumps of Ni-Resist. Bronze is also used for these pumps.

Pipelines.

Corrosion of pipelines occurs both from the material handled on the inside and from the soil attack on the outside. Little apparently can be done about the inside, but considerable studies have been made of protecting the outside by means of appropriate wrappings that shield the pipeline from contact with the soil through which it passes. Cathodic protection by means of light metal anodes, or by application of counter electric currents

* S.A.E. 2115 no longer standard.

is also applied to protect pipe-lines. In some cases the inside of the pipe is attacked only on the bottom, due to the presence of water dropping out of the cargo. In this case, the pipe is revolved through an appropriate angle at regular intervals, and the maximum service is obtained. Inhibitors are being studied in an effort to lessen the attack from water in the bottom of the pipe.

In the matter of the handling of gases, considerable corrosion has been experienced in the compressors. This is being combated by the use of suitable alloys in the linings and in the valves. Ni-Resist cast iron has apparently done an excellent job as the liners of compressors handling sour gas; it and various other corrosion-resistant materials are employed in the valves. At the present time a rather elaborate installation of all Monel valves is under test in a rather corrosive field. Sufficient time has not elapsed to evaluate these valves in terms of corrosion resistance.

The favourite alloy steel for pipelines is the carbon–manganese alloy of about 0·25 per cent carbon, 1·25 per cent manganese. This steel develops 70,000 to 75,000 p.s.i. ultimate strength and has an endurance limit of about 30,000 to 35,000 p.s.i. It apparently responds readily to welding by a variety of processes and the properties in the weld usually match those of the plate.

Refining of Petroleum.

General.

The viewpoint concerning the application of corrosion-resistant alloys in petroleum refineries has undergone some change during the last few years. Prior to the last war, the corrosion-resistant alloys, with the exception of Admiralty tubes and possibly lead linings, were largely installed as an item of maintenance. The common practice was to buy equipment designed for a year of service and then to install resistant materials in locations where corrosion had become evident. Much lining of existing towers took place under this schedule. The practice continues to exist and will continue for many small units of refining.

In the case of large units, the practice of awaiting corrosion before taking action is impractical and costly. For instance, when a refinery depends upon one or more topping units of large capacity, say, 50,000 brl/day or more, for feed for other units, it is imperative that these units operate continuously and efficiently. Long operational life is now also expected from cracking and other units.

The result of expecting runs of long duration from equipment has resulted in a wide use of corrosion-resistant material in new equipment. In order that the resistant material shall be effectively and economically applied, it has become necessary to organize groups in refineries to study corrosion. These groups have so well mastered their art that they can, in many cases, specify correct materials for the variety of corrosives encountered. Their studies are endless, however, since new methods and new reagents constantly appear.

In order to review the metallurgical progress made in refineries, it is well to examine the needs that exist and the solutions offered.

Since the metallic requirements in a refinery vary with temperature more than any other condition, it seems advisable to study the requirements

at varying temperature levels. With the proposal to form gasoline from natural gas by partial oxidation of methane by oxygen from the air, metal temperatures have been depressed to −320° F in the location where oxygen is secured. The formation of hydrogen from refinery and natural gases involves temperatures of 1600 to 1800° F, as do the use of tube supports in fired coils. All intermediate temperatures are employed. Thus a wide range of metal temperatures are encountered in a refinery.

The following discussion will take up in order the ranges of low, intermediate, elevated, and high temperatures. Low temperature will be considered as 0° F and below; intermediate from 0° F to 500° F. This range is the one where electrolytic corrosion can occur. Elevated temperature will cover 500° F to 1300° F, the region of sulphur and organic (naphthenic) attack. High temperature will consider 1300° F to 1800° F and above. Creep of metal is a factor in the last two ranges.

Low Temperature (0° F *and Below*).

There are a number of locations in refineries where low temperatures are employed, as in dewaxing operations, controlling of reactions, liquefaction, and fractionation of gases. Storage of gases in liquid form and fractionation of air previously referred to may also be included.

It is the consensus among engineers that impact value is the most useful property for evaluating a metal for sub-zero uses. The common practice in the United States is to require a minimum value of 15 ft.-lb. (Charpy, keyhole notch) of a metal for use at sub-zero temperatures when it is an important part of a piece of equipment. The 15 ft.-lb. must be obtained at the minimum temperature of service. The requirement applies that the minimum value must be obtainable from critical locations as from welds and adjacent material. The direction of the notch of the specimen in relation to major stress is specified in the codes for vessels.

The two vessels in Fig. 16 are indicative of the need for impact resistance at sub-zero temperatures. The carbon steel vessel and the 8·5 per cent nickel steel vessels were reported as cooled to about −310° F and struck with a 6-lb. hammer. The carbon steel vessel failed as shown. Vigorous striking, both with a 6-lb. and a 16-lb. hammer, failed to crack the 8·5 per cent nickel steel vessel and only caused the indentations shown. From Charpy impact tests of heats of the compositions of the vessels, it was demonstrated that the carbon steel would possess little or no impact value at −310° F, while the 8·5 per cent nickel steel would give in excess of 20 ft.-lb. at the low temperature.

A number of primary metals, such as aluminium, nickel, Monel, copper, and the precious metals (usually metals with face centred crystal structures), retain at sub-zero temperatures a high order of their impact value as determined at room temperature. A large number of alloys of copper and of nickel also possess this property as well as the austenitic steels.

The ability of steels to maintain at sub-zero temperatures a fair order of their room temperature impact value appears to depend upon heat treatment and upon nickel content. It seems that most ferritic steels that are fully hardened throughout and subsequently drawn possess good impact values at very low temperatures (Table IX).[7] This is of interest from the standpoint of valves, fittings, and relatively small parts.

TABLE IX.

Average Impact Properties of Several S.A.E. Steels Drawn to Approximately 200 B.H.N.

Heat treatment and hardness.					Energy absorbed in ft.-lbs. at indicated temperatures.							
S.A.E. no.	Quenching temp., ° F.	Quenchant.	Rockwell C after quench.	Drawing temp. ° F.	B.H.N. after draw.	−190° C. or −310° F.	−90° C. or −130° F.	−70° C. or −94° F.	−55° C. or −67° F.	−40° C. or −40° F.	−10° C. or +14° F.	+20° C. or +68° F.
4130	1575	Water	48·5	1260	207	(6) 6·4	(2) 116·9	(6) 119·8	—	(6) 119·8	—	(3) 119·8
4140	1575	Oil	42·5	1240	228	—	—	(6) 72·0	(3) 112·7	(6) 106·9	(3) 117·2	(3) 111·2
4615	1525	Water	42·5	1100	235	(6) 8·1	(3) 119·8	(6) 119·9	—	(6) 119·8	—	(3) 119·9
4640	1525	Oil	44·5	1240	217	(6) 10·7	(3) 71·3	(6) 78·1	—	(6) 105·7	—	(3) 109·9
4815	1475	Oil	37·5	1100	228	(6) 25·3	(3) 117·9	(5) 119·8	—	(6) 119·8	—	(3) 119·8
4340	1525	Oil	45·0	1260	228	—	—	(5) 38·5	—	(6) 73·8	(3) 75·5	(3) 93·5
C–Mo *	1625	Water	36·0	1100	228	—	—	(5) 55·4	—	(6) 77·0	(6) 102·8	(6) 71·0
2330	1450	Oil	40·0	1050	217	(5) 10·4	(3) 95·9	(6) 108·9	—	(6) 104·9	—	(3) 106·2
3135	1500	Oil	45·0	1200	217	—	—	(5) 31·5	(3) 105·2	(6) 109·2	(3) 118·2	(3) 113·8
3240	1475	Oil	44·5	1240	223	(6) 7·8	(3) 81·5	(5) 103·9	—	(6) 113·8	—	(3) 114·4
6145	1525	Oil	44·5	1250	228	—	—	(6) 38·5	(3) 106·2	(6) 101·0	—	(3) 102·6
1045	1525	Water	40·0	940	228	—	—	(6) 7·6	—	(6) 11·4	(3) 33·5	(3) 38·2

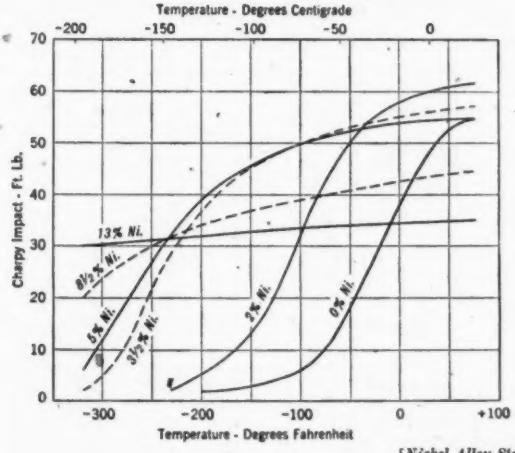
[Data: *Metals and Alloys*, April 1938.

* Analysis: C 0·15%; Mn 1·00%; Si 0·22%; Mo 0·47%.
Figures in parentheses indicate number of breaks used to compute average.
Note.—Charpy V Notch used per A.S.T.M.—1937 (Fig. 1*a*) p. 1510.

See Table II for analyses of many of the steels mentioned in this table.

Normalized plates and parts are required for large structures, and here the retention of impact value apparently depends largely upon the nickel content (Fig. 17).[8] Grain refinement can be utilized to a certain extent in the case of carbon steels to provide a good order of impact values for temperatures down to about −50° F. The regions of the welds in vessels made from specially treated carbon steels represent critical areas, since the structure must not be greatly disturbed by welding if a high order of impact value is to be maintained. It is generally considered advisable to use nickel steels for the important vessels in petroleum refineries that are intended for service at sub-zero temperatures.

The 2 to 3 per cent nickel steels have been found adequate from a retained impact value standpoint for temperatures down to −100° F. These steels



[*Nickel Alloy Steel Data Book.*

FIG. 17.

EFFECT OF NICKEL CONTENT ON THE RESISTANCE TO LOW TEMPERATURE EMBRITTLEMENT OF NORMALIZED LOW CARBON STEEL (KEYHOLE NOTCH). ALL STEELS CONTAIN 0·1% CARBON EXCEPT NO. 1020 (0·2%) AND THE 2% NICKEL STEEL (0·15%).

have been widely used in connexion with dewaxing operations. For temperatures down to −160° F the 3·5 per cent nickel steel with 0·20 per cent max carbon is used (Fig. 18), and for certain applications at this temperature level the austenitic stainless steels have been used. However, their use was considered more of a war necessity than the dictates of sound economy. Below the temperature level of −160° F, the most satisfactory steels from the standpoint of retained impact value are the austenitic stainless steels or possibly the newly developed 8·5 per cent nickel steel. If selection falls upon non-ferrous metals, nickel, Monel, aluminium, copper, and alloys of nickel–copper will all be found to have a high order of impact value at the lowest obtainable temperatures. Tables X and XI[9] contain information relative to nickel, Monel, and Inconel at sub-zero temperatures.

In general there are in existence to-day a large number of materials quite satisfactory from the standpoint of high impact value at sub-zero

TABLE X.

Short-time, Low-temperature Tensile Properties.

Material.	Condition.	Temperature, ° F.	Yield strength (0·20% offset), p.s.i.	Tensile strength, p.s.i.	Elongation in 2 inches.	Reduction of area, %.
Monel	Forged	70	67,000	92,000	31·0	72·7
		−297	91,500	128,250	44·5	71·8
		−423	96,400	142,000	38·5	61·0
	Annealed	70	31,300	78,650	51·5	75·0
		−297	49,500	115,250	49·5	73·9
Nickel	Hot-rolled	70	24,600	65,600	—	—
		−112	27,500	76,400	—	—
		−292	28,000	98,000	—	—
		−310	—	103,000	51·0	—
Inconel	Hot-rolled	70	—	87,000	42·5	71·9
	Hot-rolled	−315	—	116,750	51·0	72·7
	Cold-drawn 50% reduction	70	—	145,000	10·0	35·1
		−315	—	182,000	10·0	49·5

TABLE XI.

Charpy Impact Strength—ft.-lb.

Material.	Condition.	Temperature, ° F.		
		Room.	−112.	−310.
Nickel	Annealed	216	235	234
	Hot-rolled	195	236	227
	Cold-drawn	185	205	210
Monel	Annealed	216	219	212
	Hot-rolled	219	213	212
	Forged	216	—	216 *
	Cold-drawn	181	178 †	—
	Cast	74	—	90
	Weld metal	78	—	73
K-Monel	Cold-drawn and age-hardened	27	27 †	—
H-Monel	Cast	44	—	47
Inconel	Annealed	236	206	187
	Hot-rolled	213	—	169 ‡
	Cold-drawn	69	—	61 ‡

* At −297° F. † At −110° F. ‡ At −315° F.

temperatures, and the choice of a material is usually dictated by economics or by some structural consideration. For instance, in addition to high impact value, the austenitic stainless steels possess a high order of tensile strength and a high melting point and are useful where these properties are considered also desirable. Nickel and Monel share these properties.

The 8·5 per cent nickel steel with 0·12 per cent max carbon, which was fairly recently developed in the laboratories of The International Nickel Company, offers in addition to high ultimate strength a high yield point with good elongation values. The newness of this steel has prevented a background of experience being available; however, it is anticipated that it will eventually take its place as one of the steels for use at sub-zero temperatures.

The question is often raised as to the effects of a long time exposure to sub-zero temperatures upon the impact value of materials that have been found suitable as a result of short time exposure and testing. A partial answer is contained in a paper by T. N. Armstrong and A. J. Miller,[10] and these results are summarized in Table XII. They seem to indicate that there is no deterioration of 25 chromium 20 nickel, 18 chromium 8 nickel, or the 8·5 per cent nickel steel, as a result of exposure to liquid

TABLE XII.

Charpy Impact Values—ft.-lb. (Keyhole Notch).

		Material.			Plate material.	
		8·5% nickel welded with 25–20, notched in weld.	8·5% nickel welded with 25–20, notched in fusion zone.	18–8 welded with 18–8, notched in weld.	8·5% nickel.	18–8.
Tested at 70° F	No aging, no chilling	24, 25	28, 29	28, 28	50, 51	80, 90
	No aging, chilled −320° F	27, 30	53, 31	31, 33	43, 44	90, 91
	Aged 6 months at 70° F, no chilling	31, 29	36, 50	26, 23	53, 50	96, 97
	Aged 6 months at −320° F	25, 30	50, 29	35, 26	42, 43	91, 83
	Aged 12 months at 70° F, no chilling	24, 28	46, 42	35, 31	50, 52	93, 92
	Aged 12 months at −320° F	28, 33	35, 40	28, 29	44, 43	89, 83
Tested at −320° F	No aging	26, 19, 27	22, 30, 28	18, 18	25, 24	72, 73
	Aged −320° F, 6 months	20, 16, 17	28, 20, 32	22, 22, 17	26, 22, 24	72, 74, 75
	Aged −320° F, 12 months	27, 21, 18	26, 27, 24	22, 19, 17	23, 23, 23	73, 77, 74

nitrogen temperature (−320° F) for a period of 1 year. It will be noted that samples were tested at the end of 6 months and also at the end of the year, and that there seems to be no trend away from the results obtained at the start of the test.

The matter of melting point is one of considerable interest in a refinery, especially in the case of valves and fittings. Often the presence of a high-melting-point material will aid in confining a fire to a given area. The austenitic stainless steels—nickel and Monel—represent commercial materials possessing high impact values at sub-zero temperatures, and also possessing high melting points—*i.e.*, above 2300° F. These materials, therefore, suggest themselves as valves and fittings in lines serving at sub-zero temperatures, and are so used.

Tubing of 3, 5, and 8·5 per cent nickel suitable for low temperature uses is on the market in the United States. The austenitic stainless steels—nickel, Monel, brass, copper, and aluminium—are all available in tubular form and can be used at sub-zero temperatures.

Intermediate Temperature Range (0° *to* 500° F).

Within the temperature range 0° to 500° F much of the corrosion in a refinery takes place and is electrolytic in nature where water is present. Equipment operating within this temperature range contains much of the corrosion-resistant materials found in a refinery.

(a) *Linings for Vessels.*

The lining of towers is one of the most important applications for corrosion-resistant material. Table XIII lists some linings used and the

TABLE XIII.

*Some Common Metallic Linings of Refinery Vessels.**

Corrosive encountered.	Temp, ° F.	Stainless. (Table II.)	Nickel.	Monel.	Hastelloy.†	Lead.
HCl, gas	—	—	Regular	—	Alloy B	—
HCl, dilute	—	—	Regular	Regular	Alloy B	—
Caustic, conc.	650	—	L Type	—	—	—
Caustic, dilute	400	—	Regular	Regular	—	—
Hydrogen sulphide	Above 500+	410; 304; 316; 347	—	—	—	—
Hydrogen sulphide	Below 500	—	—	Regular	—	—
Furfural	300–500	410; 304; 347	—	Regular	—	—
Phenol	300–500	410; 304; 347	Regular	Regular	—	—
Naphthenic acid	Room–900	Inconel or Type 316	—	Regular (below 500° F)	—	—
Chlorinated solvents	Room–300	—	Regular	Regular	—	—
Ethanolimine	Room–400	304; 347	—	—	—	—
Sulphuric acid, conc.	—	Steel generally used.				
Sulphuric acid, dilute	Room–250	—	—	Regular	Alloy B	Used extensively (up to 85% at 400° F)

* The materials listed above are those commonly in use.
† The limited use of Hastelloy shown here is a reflection of its cost rather than upon its ability to resist the reagents. It probably resists all of them well.

corrosive encountered. Bubble towers offer an interesting study, since they operate within a range of temperatures, 500° F and above, where sulphur attack is the primary cause of destruction down to the range, 500° F and below, where attack by dilute mineral acids is the chief cause. It is not uncommon to find a change in the metallurgy of the protective material within a bubble tower (Fig. 19), since where the feed enters, sulphur attack is predominant, due to the elevated temperature, and the sulphur attack may be expected about two-thirds of the way up the tower. In the top of the tower the reflux pumped back often carries enough mineral acid to completely change the nature of the attack. Two different materials are required to combat these two types of corrosion (Table XIV).[11] In the bottom, or hotter part, a stainless steel must be used to resist sulphur. This material is of Type 410 (11 to 14 per cent chromium material), or Type 304 (18 per cent chromium–8 per cent nickel). Monel (2/3 nickel–1/3 copper) is the preferred material for lining the top of bubble towers and for the lining of the shell about one-third of the way down. The caps and trays (Fig. 20) should follow the metallurgy of the lining and are often Type 304 for the bottom and Monel for the top four to six trays.

It is quite difficult in the case of bubble towers to predict the exact location where the stainless should leave off and the Monel begin. In some of the earlier towers lined completely with stainless, the destruction of the top lining clearly outlines the limit of its usefulness. This is hardly a suggested method for determining the limit. In general, it will be found

TABLE XIV.

Corrosion Results from a Bubble Tower.

Location, temperature, ° F.	Bottom of tower, 700° F (approx.).	Top of tower, 185° F.
Metals.	Corrosion, inches.	Rates, inch per year.
Mild steel	0·033	0·091
18 chrome–8 nickel	0·00006	0·029
Monel	0·200	0·014
Inconel (80 nickel–13 chrome)	0·00015	0·035
18–8–3 molybdenum	0·00003	0·025

Note.—Injection of a base reduced corrosion rate at top of tower.

that the transition takes place where the temperature of the metal will be of the order of 500° F. Above this temperature, stainless is indicated, and below this temperature Monel. Due to the peculiarities of a bubble tower, the temperature of the lining and of the trays will not necessarily coincide, since the cold reflux may cause the tray to operate at a different

TABLE XV.

Results of Some Studies of Corrosion by Naphthenic Acids.

Temperature: 550° F.
Location: Column of vacuum unit.

Metal.	Penetration, inch per year.
Mild steel	0·0163
18 chrome–8 nickel	0·0236
18 chrome–8 nickel–3 molybdenum	0·0002 *
16 chrome–13 nickel–3 molybdenum	0·0009 *
Inconel (80 nickel–13 chrome)	0·0007 *
Monel (69 nickel–20 copper)	0·0012
Nickel	0·0006
Ni-Resist (cast iron)	0·0109
Cast iron	0·0080

* Three applicable metals. Possible sulphur attack (above 500° F) precludes Monel or nickel. Monel in use at temperature below 500° F.

temperature than that of the walls, which will be in contact with the hotter upsweeping gases. Some trials and test-pieces may be required to limit correctly the application of the two metals.

Naphthenic acids, which are very common in some crudes (notably Venezuela and certain California crudes), vigorously attack the 11 to 14 per cent chromium or the 18–8 type of stainless steel at elevated temperatures (Table XV).[11] When these acids are present, the lining and the caps

in the bottom should be of Type 316 stainless (approximately 17 per cent chromium, 14 per cent nickel, and 2 per cent molybdenum) or of Inconel (approximately 80 per cent nickel, 13 per cent chromium, 6·5 per cent iron). Either of these alloys is also highly resistant to sulphur attack.

Economics dictate in a large number of cases that the material for the construction of large vessels, such as bubble towers and other pieces of equipment, be made from steel faced with a corrosion-resistant surface. This corrosion-resistant surface is applied in the United States in a number of ways, among which may be listed cladding of steel with nickel, Monel, Inconel, and various stainless compositions by forming a "sandwich" in which the steel forms the outer layers and the resistant material the inner ones. This "sandwich" is rolled into plate and owing to the presence of a parting compound usually provides two steel plates clad to predetermined thickness with the corrosion-resistant material (Fig. 21). This process is associated with Lukens Steel Co., in the U.S.A., and with Guest Keen and Baldwin Iron and Steel Co. Ltd., in England. "Pluramelt," a widely used material of steel plate faced with corrosion resisting material, is reported to be formed by rolling an ingot made up of steel and the resistant material cast in juxtaposition in a mould. The product is associated with The M. W. Kellogg Company and Allegheny Steel Company. The A. O. Smith Corporation, one of the well-known vessel fabricators in the United States, has devised a method of installing a resistant facing by laying the resistant material upon a plate of steel over which is passed a machine that brings about a fusion—*i.e.*, resistance welding of closely spaced spots—of the back of the corrosion-resistant material and the face of the steel plate, thus providing a bond (Fig. 22). The contact is made at such intervals that the facing is considered permanently bonded to the plate and the reports from the industry have indicated that this material is very satisfactory in service, even where there is fluctuation in temperature. Another method of cladding steel with a corrosion-resistant facing has been developed by Babcock and Wilcox Co., and is reported to consist of placing a thin nickel sheet next to the steel face and placing upon this a layer or layers of the corrosion-resistant material, after which the whole is bonded together by a form of fusion welding of the face. The weld spots overlay so that there is a continuous bonding of the materials (Fig. 23 and Fig. 23A).

Quite a number of newly constructed vessels, as well as vessels in service, have been protected by installing liners. These liners are usually of two types, and in the past have consisted of strip lining with stainless steels where the vessels were to serve at elevated temperatures (Fig. 24), and spot-welded liners where the vessels were to serve at temperatures below about 500° F, and where nickel, Monel or some other material than stainless steel is used as the protective surface. The plug-welding of liners appears to be an art, and some difficulty has been experienced by leakage occurring in the region of the plugs. The sequence seems to be that owing to expansion stresses or to some form of corrosion fatigue, a crack develops in the region of a plug and leakage occurs behind the liners. However, much successful welding has taken place and a very large number of vessels are in service, especially in caustic service, which are faced with Monel or nickel applied by plug-welding in the manner indicated in Fig. 25.

Repairs to plug-welded liners offer a number of difficulties and in some

cases the trend has been to discontinue plug-welding for installing liners and to use strip-welding. This trend is based upon two considerations:

(1) The welders in the refinery have had more experience in strip-welding since the first work was done on vessels that were to be protected against sulphur at elevated temperatures;

(2) The strip-welding is considered to have been more successful from the standpoint of fewer leaks.

The second consideration, in the writer's opinion, may be erroneous and appears to be based upon the fact that leaking at elevated temperatures is not as evident, since a sulphur scale is formed, as it is at low temperatures where some material, such as caustic, is being handled and where the leaking is easily detected. Time will have to develop the accuracy of the assumption that the larger amount of welding associated with strip-welding is less conducive to leaks than the relatively smaller amount of welding associated with plugs.

In undertaking repairs of Monel or nickel linings of equipment that have been exposed to caustic, the most satisfactory method appears to be to sand-blast the surface since the caustic containing some sulphur compound, which will inevitably cause cracking during repair welding, is most difficult to remove and appears even to resist the action of acids, such as hydrochloric. Sand-blasting followed by hydrochloric washing would appear to be the most suitable procedure, and even here there is danger that the material which has leaked between the liner and the vessel cannot be removed and will result in cracking. It is probably best to clean the face in the area of the crack by sand-blasting and then to patch over this area rather than to attempt to fill in the crack with weld metal.

It has been pointed out before and is repeated here that installing of liners, especially by plug-welding, represents an art and the successful application depends upon the artist.

So extended are the uses of nickel and Monel liners in a modern refinery, and so important is the initial installation in both new and used vessels, that Mechanical Letter No. 8 [12] covering the methods of installing such liners is herewith reproduced.

APPLICATION OF NICKEL, MONEL, AND INCONEL LININGS TO EXISTING STEEL STRUCTURES.

Linings of nickel, Monel, and Inconel sheet or strip have been used with very good results for a number of years in many types of services.

Field lining of existing steel vessels with pure nickel and high nickel alloys can be done readily if certain precautions are observed in providing proper fit-up, welding skill, inspection, and testing. While a lining job cannot be accomplished in the field as cheaply as in the fabricating shop, nevertheless, field lining can be done satisfactorily and economically by various methods to be described.

Choice of Lining Thickness.

The thickness of liners has varied from 0·050 inch to $\frac{1}{8}$ inch; it is recommended that for field linings it be not less than 0·062 inch thick for floors and walls, where no overhead welding is required. Not less than 0·078 inch thick should be used for overhead work. These minimum thickness values are chosen because thinner liners require a very high degree of welding skill, as well as precision fitting. Regardless of the thickness chosen for the lining it is suggested that the men who are to do the welding be checked on their ability to weld lining material in various positions; flat, vertical, horizontal, and overhead. Particular attention should be given to those positions which will prevail on the job.

Attachment Method.

The two commonly used methods of attaching the linings to the shell in the field are generally referred to as " plug-welding " and " strip-welding."

In " plug-welding," sheets as large as can be inserted through manways, or other openings, are punched or drilled on staggered centres and then attached to the shell by plug-welding through the holes and along the edges of the sheet.

The " strip-welding " method uses narrow strips, usually 4 inches wide, which have no plug-weld holes and are attached to the shell at the edges only.

Each of the above methods has distinct advantages, but a variation of the strip method is preferred, particularly in field installations, for those services in which pressure and temperature only are to be considered. Close centre-to-centre or rigid attachment of the high nickel alloys to mild steel vessels, to eliminate excessive warpage or buckling, is unnecessary since the coefficients of thermal expansion of nickel, Monel, and Inconel are very close to that of mild steel; consequently strips 12 inches to 18 inches in width can be used when vacuum is not a factor. When vacuum must be considered, strips as narrow as 4 inches may be required. Wider strips (12 inches, 18 inches) can be used if plug-welds are provided on fairly close centres (3 inches to 4½ inches).

" Plug-Welding."

The diameter of the plug-welding hole is dependent upon the thickness of the liner sheet, as is shown in Table I. Holes which are too small may cause trouble during welding by shorting of the arc or by flux interference, while very large holes can result in excessive iron dilution in the weld metal with attendant danger of reduction of corrosion resistance and, in extreme cases, cracking of the weld. The holes should be large enough to provide for welding in two passes, the first pass being made around the periphery of the hole, which effects the required joint between liner and shell. After removal of welding slag from the first pass the hole is filled or covered by the second pass. It is suggested that tests be made on scrap material to determine the proper plug-weld hole diameter for the lining thickness to be used.

Plug-welding should always start in the centre of the sheet and progress outwardly to the edges, in order to minimize locked stresses.

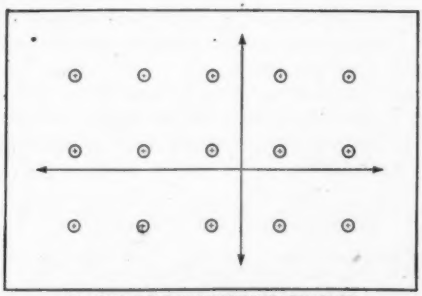


FIG. 1 PLUG WELDS TO BE MADE OUTWARDLY FROM CENTER BEFORE TACKING EDGES

Table I.

Plug-hole Diameter v. *Sheet Thickness.*

Sheet thickness.	Hole diameter.	Electrode diameter.
0·062 inch to 0·078 inch incl. . .	¾ inch	¼ inch
0·093 inch to 0·140 inch incl. . .	¾ inch	¼ inch
0·156 inch to 0·187 inch incl. . .	1 inch	5/32 inch

Some fabricators prefer to use slots, in place of round holes, for attaching linings. Suggested slot sizes are shown in Table II.

TABLE II.

Slotted Holes v. *Sheet Thickness.*

Lining thickness.	Slot size.	Electrode diameter.
0·062 inch to 0·093 inch incl.	$\frac{1}{4}$ inch × $1\frac{1}{2}$ inch	$\frac{1}{8}$ inch
0·109 inch to 0·171 inch incl.	$\frac{5}{16}$ inch × $1\frac{1}{2}$ inch	$\frac{1}{8}$ or $\frac{5}{32}$ inch
0·87 inch	$\frac{3}{8}$ inch × $1\frac{1}{2}$ inch	$\frac{5}{32}$ inch

The distance between the holes ("centres") is dependent upon the intended service and the required unit loading of the plug-welds. "Centres" may be varied from 3 inches for high loadings to 10 or 12 inches for low loadings. One imperfect plug-weld in a lining sheet can have a worse effect on the lining than if no plug-welds were used. One leaking plug-weld, in time, can allow enough water, steam, or processing liquid into the area between liner and shell to ruin that section either by corrosion or by bulging during rapid heating of the vessel. The entrapped liquid can flash into steam or vapour and create pressures capable of bulging or rupturing the liner. Tests have shown that pressures of approximately 120 p.s.i. will rupture a 0·062-inch lining when plug-welded on 4-inch centres.

ELECTRODES.

The diameter of the welding electrode to be used will depend upon the lining thickness, in accordance with Table III.

TABLE III.

Lining Thickness v. *Electrode Diameter.*

Lining thickness.	Electrode diameter.	Amperes.		
		"130X" Monel.	"131" Nickel.	"132" Inconel.
0·062 inch to 0·125 inch	$\frac{1}{8}$ inch	60– 90	85–110	85–105
0·156 inch to 0·187 inch	$\frac{5}{32}$ inch	90–150	105–150	110–130

It is important that the amount of heat input be held to a minimum consistent with good arcing characteristics. Welding speeds and heats must be controlled so as to provide adequate but minimum penetration of the weld metal into the steel shell. Better final workmanship will result if the welders are permitted to practice on scrap material before being called upon to actually apply the liners. This practice should involve welding of sheet edges and plug-welds in all positions likely to be encountered on the job.

LINING PROCEDURES.

The attachment of the individual sheets can be done by the following procedures:

(*a*) The first sheet is located in place and held tightly to the shell by means of jacks or timbers, and plug-welding completed. The edges are then tack-welded to the shell on 4- to 6-inch "centres" and the next sheet located so that the abutting edges overlap $\frac{1}{2}$ to 1 inch. When plug-welding is completed the sheet is tack-welded on all edges, and the overlapping edge welded continuously to the first sheet. This method offers some advantage in greater ease and speed of fitting, particularly where large sheets are used. This method also allows some variation in fit-up precision, which in turn can result in increased speed of lining.

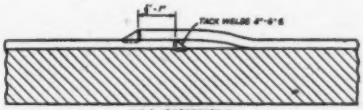


FIG. 2 PROCEDURE A

(*b*) The first sheet is located, plug- and tack-welded as described in (*a*), after which the second sheet is located leaving a gap of $\frac{1}{4}$ to $\frac{3}{8}$ inch between sheet edges. After completion of plug-welding, the peripheries of the sheets are welded continuously to the shell. Following the removal of welding slag from the two fillet welds at the adjoining edges a third weld is applied covering the fillet welds and the space between them.

Care must be exercised to avoid excessive penetration into the steel shell. It is also essential that the third or "cover" bead be built up to, at least, the thickness of the lining.

This method is not considered desirable for field work and not too satisfactory for use in the shop as it requires welding skill of the highest order.

A variation of this method involves the use of a narrow butt strap to cover the two fillet welds (tack-welds can be substituted for the continuous fillets). The butt strap is welded continuously to the adjoining sheets.

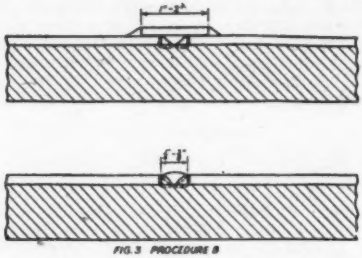


FIG. 3 PROCEDURE B

(*c*) In this method the first and second sheets are applied to the shell allowing a $\frac{1}{16}$-inch to $\frac{1}{8}$-inch gap between sheets. The edges of the sheets are attached to the shell by small, thin, tack-welds, after which the adjoining sheets are joined and attached to the shell by one continuous bead. This method is the least desirable for field welding as a weld of this type requires a high degree of welding skill to ensure complete sealing of both sides of the joint and adequate penetration into the steel.

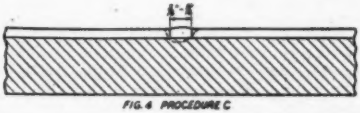


FIG. 4 PROCEDURE C

(*d*) The first sheet is applied, plug-welded and welded on the edges. The welding slag then is removed and the weld is trimmed by chipping, on the edge contacting the steel shell, to remove any bumps caused by restrikes, and to provide a fairly straight line. The edge of the adjoining sheet is fitted to the trimmed weld edge, tack-welded in place at this edge only, and the plug-welding completed. After plug-welding, the remaining three edges should be tack-welded to the shell. The joint between the sheets is then welded continuously, with the second weld overlapping the first bead. This method is preferred because the welds involved are relatively narrow and the opportunity for dilution of the weld metal with iron is minimized. The possibility of leakage is also reduced greatly.

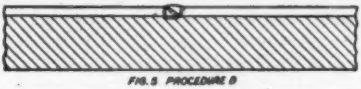


FIG. 5 PROCEDURE D

Strip-Welding.

When the linings are to be applied in relatively narrow strips the strip length should be held to a maximum consistent with good fit-up practice. The choice between

horizontal and vertical application is a matter of judgment or experience. The degree of welding skill available is also a governing factor. Fitting and welding of the edges are done following the various methods outlined for the "plug-welding" method, although it is not economical to use the lap joint method, (*a*), due to the large amount of extra metal required for lapping. The same disadvantage is applicable to the use of a cover strip. The method outlined in (*d*), above, is preferred.

Testing.

Freedom from leaks in lining welds can be confirmed by careful and thorough inspection of each weld immediately following its completion. A final pressure test is advisable. The main reason for the preference for a variation of the standard strip-welding method is that each section of the liner can be tested individually by drilling into the shell, from the outside, a hole large enough to receive a $\frac{1}{4}$-inch pipe nipple. The tapped portion of the hole should be drilled only deep enough to obtain three or four threads. The hole is then continued, using a $\frac{1}{4}$-inch or $\frac{1}{8}$-inch diameter drill, completely through the shell. Air, under pressure of 2 or 3 p.s.i., may be applied to the lining through the hole. A simple soap suds test will reveal the presence of any leaks. This, or any other method of testing, which will definitely show up leaks in the liner welds is not applicable to linings installed by the standard strip method because of the large amount of labour that would be involved.

Where linings are applied by the standard strip method it is essential that competent inspectors be charged with the examination of every foot of weld even though the weld is to be covered subsequently by a second weld.

General Suggestions.

Before applying a nickel, Monel, or Inconel lining to an existing steel vessel it is necessary that the interior surface of the vessel be thoroughly cleaned. This is accomplished best by sand- or steel grit-blasting. Any "coke," oxide, aluminium, oil grease, or other foreign matter left on the surface to be lined will cause trouble during the lining operation. It is definitely uneconomical to attempt the lining of a vessel which has not been properly prepared for welding.

When lining heads or domes in vessels, either the strip method may be used or the lining sections cut, formed, and shaped into "orange peel" sections to fit the contours snugly.

Appreciable savings in time and an increase in quality can be effected by careful detailing of the job and the provision of proper equipment for holding the sheets, or strips, tightly against the shell. Small hydraulic jacks, of the type used for automobiles, in combination with 4 × 4 inch timbers have been found to be particularly useful on lining jobs.

(b) *Condensers.*

Tubular condensers represent some of the most important and troublesome equipment in refineries. In general, Admiralty tubing is used in order to prevent corrosion on the water side, and the shells are often of steel, although in some cases they are of cast iron. In some instances an effort is made to protect the shell by introducing caustic, ammonia, or some other base into the gases entering the condenser. This practice invariably leads to the destruction of the tubing since the effort to maintain a neutral water leaving the condenser represents a task beyond the ability of the operators. A most satisfactory practice has developed and consists of providing a Monel lining in the bottom of the condenser shell and then neutralizing the acid on the outlet side of the condenser. The lining can be applied to the existing equipment (Fig. 26), or new equipment can be made up with shells suitably lined, or from Monel plate (Fig. 27).

Cast-iron shells which have been subjected to attack have been protected by a Monel lining installed by the method of drilling into the shell and placing bolts of Monel which then fit into holes punched in the liners. The bolts are welded to the liners and serve to hold it fast. The use of

Monel electrode, such as the conventional 130X, or use of the newly developed Ni-Rod, would permit attaching the liners to cast iron which has not suffered graphitization over the face to be protected.

Destruction of tubing has presented an extensive field of study and in general it will be found that all of the methods by which Admiralty tubing can be destroyed exists in one or more forms in refineries, these methods consist of dezincification, stress cracking, pitting, inlet corrosion, and impingement by air bubbles. As a commentary upon the destruction of condenser tubes in a petroleum refinery, it will be noted that what is considered satisfactory service in a condenser in a refinery in terms of months would have to be expressed in terms of years to be satisfactory performance in a land power station. For example, 11 to 15 months service in a petroleum refinery might be considered satisfactory, whereas 11 to 15 years service might be expected in the case of a power station.

Since the introduction of inhibitors, such as phosphorus, antimony, and arsenic, dezincification of Admiralty tubing has been brought well in hand, and this cause of destruction has possibly moved from first place in the case of petroleum condenser tubes to one of less importance.

Where inlet corrosion is a source of destruction, and this should be fairly rare in the case of refineries, the tendency has been to go to aluminium brass tubing or to the 70 per cent copper, 30 per cent nickel composition.

Prior to the extensive use of inhibitors in Admiralty tubing, an effort was made to circumvent dezincification by the use of an alloy high in copper and low in zinc. These were referred to as red brass tubes. These high copper tubes were so vigorously attacked by the sulphur that in most cases their life did not equal that experienced from the Admiralty tubing that was subject to dezincification at that time.

The trend in refineries is to install Admiralty tubing, and if this does not give a satisfactory life, to use some form of inhibited aluminium brass, and in the case of very severe destruction the trend is to the 70 per cent copper, 30 per cent nickel tubes.

The 70/30 copper–nickel tubes have been referred to as ones that have been applied to the so-called " hot spots," which means they have been installed in very trying locations. In general, these tubes have given excellent accounts of themselves, and their use is being extended principally because of their better resistance to impact by air released from the water and their generally better behaviour at temperatures more elevated than could be tolerated by Admiralty, It has been noted, however, that these tubes are subject to a form of sulphur attack at 400° F and above (metal temperature) not experienced by Admiralty, and that in some cases they have built up a heavy sulphide film that has served to reduce the heat transfer. The 70/30 tubes are widely used where salt water, brackish water, and contaminated salt water are employed as a coolant. A Monel bundle has been in service for about 7 years in a location where the brackishness of the water caused early destruction of Admiralty.

Tubes of two metals, bimetal tubes, have been repeatedly offered and have been explored from time to time. The logic of these tubes is excellent, since one metal such as Admiralty is offered to resist the action of water, while some other material as steel is offered to resist conditions such as the presence of caustic or ammonia. Mechanical difficulties associated with the rolling

in of these tubes have retarded their wide acceptance. Some Admiralty tubes, nickel plated on the outside, have been in test without decisive results. Caustic in the overhead product establishes a location where the plated tubes should offer advantages.

Condensers for caustic units as well as reboilers in these units extensively use Monel tubes (Table XVI). 70/30 also finds use in this service. Where

TABLE XVI.

Record of Some Monel Tubes in Caustic Service in Refineries.

Corrosive.	Service.	Size.	Service life.	Remarks.
1. Caustic plus mercaptans	Reboiler tubes, steam aver. 283° F	¾ in. × 36 inches × 14 ga.	17 months to date (steel 2-8 weeks)	Condition—good
2. Regenerated caustic outside, foul caustic (H_2S) inside	Exchanger tubes, about 250° F	1·0 inch × 12 feet × 14 ga.	3 years to date (original installation)	Condition—good
3. Foul caustic (H_2S) inside	Reboiler tubes, about 300° F	1·0 inch × 18 feet × 14 ga.	2 years to date (steel about 5 months)	Condition—good
4. Foul caustic (H_2S) outside	Reboiler tubes	—	6 years to date	Condition—good
5. Caustic soda and sodium chloride	Tubes in an evaporator. Tubes about 200° F	2 inches × 48 inches × 16 ga.	16 years	Condition—good

phenols, ethanolamines, and other organic corrosives are encountered, Monel or stainless steels are used; the waterside corrosive often dictating the choice.

A great deal of attention has been given to tube sheets for refinery condensers, and considerable interest lately has been shown in steel faced with Monel on the waterside. These sheets are made from steel which has been clad in the conventional manner, such as the method employed by Lukens Steel Co. (Fig. 21) (see also Fig. 21A), referred to previously, or in some cases the Monel has been overlaid upon the steel by means of electrodes. A third method, which is used to clad the sheets with Monel and with brass, has been to place bands of silver brazing material between the steel sheet and the corrosion-resistant material, Monel or brass. Clamps are applied and the installation placed in the furnace, where it is raised to about 1200° F, and when there are indications along the edges that the solder has melted, the installation is removed and allowed to cool. Formerly, Naval brass or other forms of copper alloy tube sheets were widely used and their use is still extensive. The trend to the clad-steel sheets has been dictated by a desire for a material with a high yield point which will permit several re-rollings before the holes in the tube sheet become so large that the sheet must be scrapped. In some refineries it is not uncommon to find a number of bundles re-tubed annually, so that this matter of expanding holes has been found to be of considerable importance.

(c) *Insulation Straps and Wires.*

The matter of retaining insulation on vessels and piping has come in for quite a lot of attention in the last year or so, with the result that the

lugs welded to vessels, the wire upon which some of the insulation is placed (referred to as chicken wire), and the outer straps are now being increasingly made of stainless steel or Monel. The very corrosive atmospheres in refineries have resulted in the early failure of brass strapping formerly used. The Monel and the stainless steel strapping both appear to give prolonged life under refinery atmospheric conditions. This is particularly important in the case of units that will stay on the line for long periods of time—*i.e.*, have long runs—although the major destruction of the "chicken wire," that holds some of the insulation in position, is reported to take place on vessels that are shut down periodically. The moisture vapours in the insulation condense and permit electrolytic corrosion to take place.

(d) *Refinery Pumps.*

The number and variety of pumps encountered in a refinery is amazing. However, when it is considered that fluid petroleum enters a refinery, is rapidly circulated through the various refining processes, and, finally, is distributed to the destination for finished products or waste, it becomes evident that variety and number is needed.

In addition to petroleum, a large quantity of water also is pumped in a refinery. Actually much more water than petroleum is handled. This is due to the fact that most refining processes are concerned with introducing heat to an oil stream and then abstracting it. No matter how efficiently the exchangers operate, there is generally a large amount of heat to be removed by water. The location upon the coast of many large refineries in the United States necessitates the handling of contaminated sea-water by the pumps supplying cooling water. Cast iron and bronzes are used in the casings of the large water-pumps, impellers of 18–8 stainless steel are reported to give oustanding service in large pumps. Monel is also used in this service as well as bronze. Due to the protective oxide film formed on stainless steels, the 18–8 impellers are at their best in fairly continuous service. This alloy is also reported to resist to a high degree the action referred to as cavitation. Cavitation is usually associated with features of design and can be largely avoided by careful design.

In some very corrosive sea-water locations, Ni-Resist cast iron is used as the casing, impeller, rings, and sleeves of water-pumps. This material is quite resistant to sea-water (Fig. 28).

In general, Ni-Resist is one of the most useful alloys for use in refinery pump parts exposed to corrosion. This alloyed cast iron is used to resist corrosion from salt water, brines, corrosive petroleum fractions, especially reflux from light cuts, and acids such as sulphuric and dilute hydrochloric; also bases such as caustic and ammoniacal solutions. It is found in reciprocating pumps as liners, rings, pistons, and valve seats. In centrifugal pumps as casings, impellers, wear rings, and sleeves. Pumps so equipped can generally handle any refinery product at the temperature level considered in this section, 0° to 500° F. The composition and properties of the various grades of Ni-Resist are given in Table XVII.[13] Casting difficulties have limited the use of Ni-Resist.

Table XVIII outlines the specifications of a well-known refinery pump. The corrosion resistance and hardness obtainable from the 11 to 13 per cent chrome alloy justifies its use here and in other locations.

TABLE XVII.[13]

Composition and Physical Properties of Ni-Resist.

	Type 1.	Type 1A. High strength.	Type 2. 20% nickel.	Type 2A. High strength.	Type 2B. Heat resisting.	Type 3. 30% nickel.†	Type 4. Heat and stain resisting (30–5–6).	Type 5.†
Total carbon	3·00 max	2·80 max	3·00 max	2·80 max	3·00 max	2·75 max	2·60 max	2·40 max
Silicon	1·00– 2·50	1·50– 2·75	1·00– 2·50	1·50– 2·75	1·00– 2·50	1·00– 2·00	5·00– 6·00	1·00– 2·00
Manganese	1·00– 1·50	1·00– 1·50	0·80– 1·50	0·80– 1·50	0·80– 1·50	0·40– 0·80	0·40– 0·80	0·40– 0·80
Nickel	13·50–17·50	13·50–17·50	18·00–22·00	18·00–22·00	18·00–22·00	28·00–32·00	29·00–32·00	34·00–36·00
Copper	5·50– 7·50	5·50– 7·50	0·50 max	0·50 max	0·50 max	0·50 max	0·50 max	0·50 max
Chromium	1·75– 2·50	1·75– 2·50	1·75– 2·50	1·75– 2·50	3·00– 6·00*	2·50– 3·50	2·50– 5·50	0·10 max ‡
Tensile tests: p.s.i.—Conforming to A.S.T.M. Standard Specification A–48–41 or A–126–30.								
Tensile strength, min	25,000	30,000	25,000	30,000	30,000	25,000	25,000	20,000
Machinability	Good	Good	Good	Good	Poor *	Good	Good	Good

	200° F.	500° F.	800° F.
Grey iron	5·6– 6·7	6·5– 7·3	6·9– 7·5
Ni-Resist Types 1 and 2	9·5–10·3	10·3–10·7	10·3–10·7
Ni-Resist Type 3	3·4– 4·3	5·9– 6·6	7·2– 7·6
Ni-Resist Type 4	7·3– 7·7	7·9– 8·3	8·4– 8·8
Ni-Resist Type 5	2·2 ‡	4·2– 4·5	5·9– 6·1

* Where some machining is required, the 3·0–4·0 chromium level is recommended.

† Range of Expansion Coefficients: Mean coefficient of expansion in millionths per deg. Fahrenheit from 50° F to indicated temperature.

‡ For higher hardness and greater strength, the chromium may be 2·5–3·0%, at the expense of increasing expansivity to 3·1 up to 200° F.

Table XIX is a list of applications of resistant alloys for pumps that is based on the writer's experience.

TABLE XVIII.

Liquid End Materials of Some Standard Refinery Pumps.

Types.	
Centrifugal.	**Reciprocating.**
Temperature—to 850° F. Pressure—to 750 p.s.i.g.	Temperature—to 800° F. Pressure—to 750 p.s.i.g.
Casing and head—Type 45 iron * or carbon steel. Impeller—Type 45 C iron; carbon steel or 11–13 chrome steel. Casing wear rings—Ni-Resist C iron.† Shaft—S.A.E. 4140 Steel.‡ Shaft sleeve—11–13 chrome steel or "Stellited" S.A.E. 1020.‡ Throat bushing—Ni Resist. Seal case—11–13 chrome steel. Gland—bronze. Casing bolts—S.A.E. 3140.‡	Cylinder—cast steel. Cylinder heads—forged steel. Cylinder liners—Ni Resist.† Pistons—cast iron. Piston rings—hammered iron. Piston rods—chrome alloy. Valves—chrome alloy steel. Valve seats—chrome alloy steel. Valve stems—chrome alloy steel. Valve covers—forged steel.

* 45,000 p.s.i. min tensile. † See Table XVII. ‡ See Table II.

Note.—For special corrosives parts are of special materials furnished.

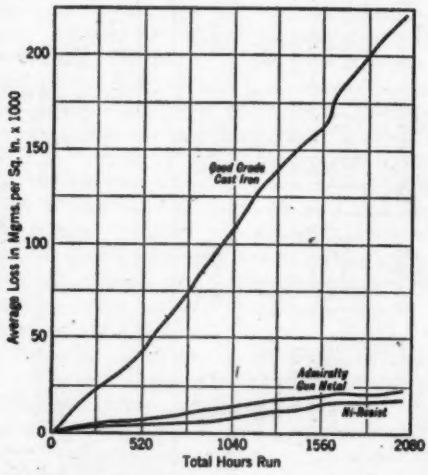


FIG. 28.

CORROSION RATE OF NI-RESIST COMPARED WITH CAST IRON AND GUN METAL IN AERATED SEA WATER. (*Metallurgia*, 1933, **8**, 45.)

(e) *Corrosives Encountered* (0° F–500° F).

The frequent existence of an electrolyte within this temperature range makes it the one most subject to corrosion. Acids and bases are employed within this range as part of the refining technique; these contribute to corrosion and necessitate resistant materials.

TABLE XIX.

Suggested Parts for Centrifugal Pumps in Petroleum Refineries.

Parts.	Choice.	Salt or brackish water.	Distillates; reflux and all petroleum products not over 500° F.	Hot-oil pumps above 500° F.	Cold, dilute sulphuric also caustic.	Hot sulphuric acid.‡	HCl.	Hydrofluoric acid hot or cold.
Impellers	1	Monel; 18–8 *	Ni-Resist	18–8 (304)	Ni-Resist	Hastelloy B or similar composition	Hastelloy B or equivalent composition for all parts.	Monel
	2	Ni-Resist	S-Monel †	18–8–2 (316)	Monel			Bronze
	3	Bronze	Bronze	(Use 316 if naphthenic acid present)	Cast iron			Ni Resist
	4	Cast iron	Cast iron		Bronze			Cast iron
Shaft	1	K-Monel	K-Monel	Inconel	K-Monel	Hastelloy B		K-Monel
	2	Monel	Monel	18–8 (304)	Monel			
Sleeves	1	Monel	Monel	Use same as shaft	Monel	Hastelloy B or D		Monel
	2	18–8	Monel		Ni-Resist			
	3	Bronze	Bronze		Bronze			
Wear rings	1	S-Monel	S-Monel	Stellite	S-Monel	Hastelloy D		S-Monel
	2	Ni-Resist	Ni-Resist		Ni-Resist			
	3	Bronze	Bronze		Bronze			
Casing	1	Ni-Resist	Ni-Resist	Steel, lined with 18–8 if possible	Ni-Resist	Hastelloy B or D		Monel
	2	Bronze	Monel		Monel			Steel
	3	Cast iron	Steel or cast iron		Bronze			

Suggested Parts for Reciprocating Pumps in Refinery Service.

Liners	1	Ni-Resist	S-Monel	4–6% chrome	Ni-Resist	Hastelloy B or D or equivalent (also body)	Hastelloy B or equivalent composition for all parts.	Monel
	2	S-Monel	Ni-Resist	*Note.*—These pumps are a special case	Monel			S-Monel
	3	Brass	Bronze		Bronze			
Pistons	1	Ni-Resist	Ni-Resist	4–6% chrome	Ni-Resist	Hastelloy B or equivalent		Monel
	2	Monel	Monel		Cast iron			
	3	Cast iron						
Rings	1	Monel §	Monel	12–14% chrome alloy	Ni-Resist	Hastelloy B		Monel §
	2	Ni-Resist	Ni-Resist		Monel §			
Rods	1	K-Monel ‖	K-Monel ‖	18–8 (304)	K-Monel ‖	Hastelloy B or equivalent		K-Monel ‖
	2	Monel		Plungers of high chrome alloy	Monel			Monel
	3							
Valves	1	Durabla type; Monel	Durabla type of Monel	18% chrome	Durabla type of Monel	LaBour or Hastelloy B or equivalent		Monel or
	2	or Ni-Resist seat		½% carbon				S-Monel
	3							

* Preferred if water aerated.
† Use where abrasion a problem.
‡ Actually the high silicon irons as "Corrosion" or "Duriron" are most resistant; their brittleness calls for special design.
§ Monel rings should be "Spring Temper."
‖ K-Monel rods should be fully hardened.

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It may be well at this time to summarize some experience gained to date from corrosion studies in petroleum refineries. The following are based on observations and on studies of corrosion by means of specimens of metals:

(1) Above about 500° F sulphur attack is the source of major corrosion and is best resisted by chromium-containing alloys. This observation is out of place here and will be made in the next section where temperatures above 500° F are considered.

(2) Below about 500° F corrosion is largely electrolytic in nature and is best resisted by non-ferrous materials. While stainless steels may show a low overall rate of corrosion, they will show a marked tendency to pit. This is due to the absence of oxygen or to other film-forming reagents. When the initial film of a stainless steel is injured under the conditions being considered, the injured part is quite anodic to the remaining film, with the result that pitting takes place readily and is a major means of destruction of stainless in many refinery locations. Reducing acids, such as hydrochloric and sulphuric, act rapidly to destroy stainless steel linings. A case was noted where three exchanger shells exposed to vapours with hydrochloric present were lined with Monel and the fourth with 18–8 stainless. The stainless liner was rapidly destroyed as well as the plate beneath it, whereas the Monel did excellent service in this, its better suited, environment. At high temperatures under sulphur attack the results would have been quite reversed.

(3) The 18 per cent chromium, 13 per cent nickel, 2 per cent molybdenum alloy (Type 316) is one of the most widely useful stainless steels entering refinery service. It resists organic acids, sulphur dioxide (sulphurous acid), carbon dioxide solutions, weak mineral acids, sulphur attack, and sea-water to a good degree.

(4) Monel (2/3 nickel, 1/3 copper), as a result of its good mechanical properties, welding qualities, and corrosion resistance, is one of the most useful non-ferrous materials entering refinery service within this temperature range. Admiralty metal, as tubing, is the most extensively used non-ferrous alloy.

(5) Ni-Resist cast iron is an extremely useful form of cast iron and is viewed as one of the most generally useful materials where a demand exists for a corrosion resistant material with mechanical properties as obtained for a low strength cast iron.

(6) The high silicon cast irons (11 to 13 per cent Si) are the most resistant to sulphuric acid, regardless of temperature or contamination, of any metallic material entering a refinery. Their brittleness is a factor limiting their use. The high silicon–nickel alloy, Hastelloy D (Table III), somewhat circumvents the low strength and fragile nature of the silicon irons. The overall resistance of the nickel alloy is not as good as the iron silicon type, and a critical corrosion range in sulphuric acid appears for this alloy at about 50 to 55 per cent acid at 350° to 400° F.

(7) Lead is resistant to sulphuric acids at most of the concentrations used in refineries. It must often be faced with chemical tiles or bricks to protect it from temperatures that might cause it to " creep ".

(8) The 70/30 copper–nickel tubes are increasingly being used, especially to resist the action of contaminated salt water. This alloy is also less subject to destruction than Admiralty from the bases used in some refineries in overhead streams. The 70/30 alloy was formerly used where dezincification of Admiralty was a source of destruction. The use of inhibitors in Admiralty has removed this cause of failure.

The theory of galvanic corrosion often provides a *pons asinorum* for the students of corrosion. The student of the theory of corrosion often reaches the galvanic theory and becomes obsessed with the idea that he is provided with an ample explanation for all of the varied types of corrosion he encounters. The hardened worker in a plant, having noted the installation of brass valves in steel lines, and contact of many dissimilar materials without deleterious effects, is inclined to view the theory of galvanic corrosion as so much scientific "moon dust." Steering a middle course is beset with a number of difficulties as will be evident from the following:

There has been offered to the chemical industry a corrosion resistant material which is largely carbon. The "nobility" of carbon to most materials has been largely recognized, and some tests were made in the research laboratory of The International Nickel Company Inc. in which this carbonaceous material was coupled to several notable corrosion-resistant materials in an acid to which the alloy would normally be fairly resistant. As was expected, the rates of corrosion for the alloys were enormously increased with one notable exception, Hastelloy D, in sulphuric acid, in which case the rate was decreased. As another example, carbon rings have been installed in a nickel-clad vessel in the presence of 50° Baumé caustic at a temperature in the vicinity of 300° to 350° F. While the carbon is normally quite noble to the nickel, in this environment an impervious film appears to be built up on the nickel, and in spite of the high potential and greater area of the carbon rings, no appreciable attack has taken place upon the nickel lining. In the presence of a less favourable reagent, the chances are the nickel would be destroyed. As a third example, Monel is considered noble to Admiralty, yet Monel is used regularly as cladding for tube sheets in condensers utilizing sea-water (Fig. 21A) and apparently to date has not harmed the Admiralty tubing rolled into the tube sheets. This type of installation is becoming increasingly popular in refineries located on the sea-coast.

Galvanic corrosion is a complex subject involving relative areas, potentials, resistances, and the effect of the particular electrolyte. It can lead to destruction of the less noble metal, and, in general, must be guarded against. It must be realized, as indicated in the examples cited, that factors other than potential must be considered. For metal to be removed in a cell, a current must flow, and the resistance to its flow may be the controlling factor as in the case of graphitized cast iron, in which the resistance in the spongy deposit will slow down the reaction.

That galvanic effects can be usefully employed is widely recognized in the case of galvanized steel in which zinc is so placed as to invite and to suffer from attack in order that the iron be spared. Monel bolts in cast-iron flanges have been protected from corrosion in sea-water. Some such bolts have been removed in good condition after 22 years service.

The vaster area of the cast iron and its protective, graphitized surface have served to protect it during contact with the Monel so that greatly increased corrosion apparently did not take place.

The following is a detailed account of the behaviour of some materials in the reagents encountered in refineries.

(1) *Sulphuric Acid.* Sulphuric acid is one of the oldest and most widely

TABLE XX.

Corrosion of Hastelloy B in 45% H_2SO_4 *at* 250° F (1725 *r.p.m.*).

C.P. sulphuric acid	0·033 inch per year.
C.P. sulphuric acid plus 1·54 g.p.l. $CuSO_4$	1·339 inch per year.

used reagents in petroleum refining. It is used to remove sulphur, to improve colour, to act as a catalyst, and as a selective solvent.

Lead is the most generally used metal to resist the corrosion of sulphuric acid. Its tendency to creep at elevated temperatures, above about 250° F, has somewhat limited its use. The practice of placing chemical tile as an insulator between the lead and the hot solution has alleviated the tendency to creep in many cases by keeping the temperature of the lead lower than that of the solution.

The high silicon (11 to 13 per cent silicon) cast irons have demonstrated

TABLE XXI.

Laboratory Corrosion Tests in 65 *and* 85% *Sulphuric Acid Plus Hydrocarbon.*

Tests made in mixtures of 15% by volume hydrocarbon solvent plus 85% by volume of corresponding acid to represent mixtures of acid and hydrocarbons encountered in petroleum refineries. Solutions stirred to keep hydrocarbon in suspension.

Temperature : 24° C (75° F).
Duration of Tests : 20 hours.

Material.	Corrosion rate, inch per year.	
	65% H_2SO_4 plus hydrocarbon.	85% H_2SO_4 plus hydrocarbon.
Monel	0·004	0·004
70–30 copper–nickel	0·007	0·008
18–8 Mo stainless (Type 316)	0·093	0·023
Hastelloy B	0·003	0·001
Hastelloy C	0·0002	0·001
Illium R	0·003	0·003
Ni-Resist	0·005	0·11

the highest order of resistance to sulphuric acid of varying concentrations, temperature, and contaminants of any material investigated to date. The well known and understood brittleness of this alloyed iron limits its usefulness.

The presence of copper sulphate in solution can greatly increase the corrosion by sulphuric acid. The laboratory of The International Nickel Company was asked to help determine the cause of the increased corrosion of 45 per cent by weight of sulphuric acid upon many of the most renowned resistant alloys made in America. The cause was traced to the presence of copper in the acid stream. Table XX shows the effects of dissolved

copper upon the corrosion rate of Hastelloy B. The results are typical of those observed in the study referred to above. It was noteworthy that the copper did not appreciably increase the corrosion rate of the high silicon iron tested at the time. The rate of corrosion of the high silicon

TABLE XXII.

Plant Corrosion Test in 70% Sulphuric Acid Plus Butane and Gasoline Polymer.

Test made in final settler vessel in connexion with polymerization of butylene. Pressure 150 p.s.i.

Temperature: 82° C (180° F).
Duration of test: 162 days.

Material.	Corrosion rate, inch per year.
Monel	0·004
Nickel	0·001 *
Inconel	0·011
Copper	0·023 †
Silicon bronze	0·024 †
Hastelloy A	0·001
Mild steel	0·039 ‡
Ni-Resist	0·007
Cast iron	0·095

* Pitted to maximum depth of 0·008 inch.
† Perforated by pitting. Original thickness 0·031 inch.
‡ Perforated by pitting. Original thickness 0·062 inch.

TABLE XXIII.

Plant Corrosion Test in 45 to 65% Sulphuric Acid Plus Hydrocarbons in Butylene Extraction Process.

Test made in bottom section of sulphuric acid regeneration tower of *iso*butylene extraction process.

Temperature: 38–116° C (100–240° F).
Duration of Test: 14 days.

Material.	Corrosion rate, inch per year.
Monel	0·080
Aluminium bronze (13% Al)	0·045
Copper	0·16
Hastelloy A	0·045
Hastelloy B	0·040
Hastelloy C	0·065
Hastelloy D	0·071
Illium G	0·10
Ni-Resist	0·67
14·5% silicon cast iron	0·002

irons was negligibly low in all cases. Tables XXI to XXVI outline some studies of materials in sulphuric acid.

Aluminium bronzes containing 10 per cent aluminium are highly resistant to sulphuric acid and find application in pumps, valves, and fittings.

The copper–silicon alloy, Everdur, finds considerable application as pipe and fittings in acid lines of refineries.

TABLE XXIV.

Laboratory Corrosion Tests in 65% Sulphuric Acid.

Test specimens rotated at 1725 r.p.m. giving velocities of 200 to 1000 feet per min depending on distance from centre of rotating shaft. No air added.

Temperature : 150° C (300° F).
Duration of tests : 18 hours.

Material.	Corrosion rate, inch per year.
S-Monel	1·3
Aluminium bronze (10% Al)	1·1
Hastelloy B	3·7
Hastelloy D	0·20
Illium G	0·82
Durimet T	>5·2 *
Worthite	16·3
14·5% silicon cast iron	0·0006

* Specimens destroyed by corrosion.

TABLE XXV.

Plant Corrosion Test in Sulphonation of Phenol with 98% Sulphuric Acid.

Test made in sulphonation kettle during twenty batches, of 12·5 hours each. Water added during last half-hours of batch. Make 180 batches per year.

Temperature : 120° C (248° F).
Duration of test : 40 days (20 batches).

Material.	Corrosion rate, inch per year.	
	Based on continuous exposure, 24 hr/day, 365 days/year.	Based on 180 batches per year.
Monel	0·020	0·005
Nickel	0·046	0·012
Inconel	0·061	0·016
18–8 stainless (Type 304)	0·24	0·062
18–8 Mo stainless (Type 316)	0·54	0·14
18–8 Mo stainless (Type 317)	0·54	0·14
25–12 stainless (Type 309)	0·18	0·047
25–20 stainless (Type 310)	0·15	0·040
Hastelloy A	0·023	0·006
Hastelloy B	0·008	0·002
Illium R	0·027	0·007
Durimet 20	0·031	0·008
Chemical lead	0·012	0·003
Mild steel	1·0	0·26

Monel is extensively used in connexion with sulphuric acid. Fig. 29 shows the corrosion rates in varying concentrations of acid at a temperature level of 203° F. It finds application as conveying lines for acid and products, as the lining of equipment in isomerization units, and as valves and fittings. It is also used as centrifugal bowls in acid treating. The presence of chloride salts in the cut of oil being treated has resulted in one case in early destruction of some of these bowls, as hydrochloric acid was generated and the combination of acids was too corrosive for the Monel.

Pump parts are made from the various resistant alloys, such as the

TABLE XXVI.

Plant Corrosion Test in Sulphonation of Organic Base.

Test made in liquid in sulphonating autoclave under 260 p.s.i. pressure. Mixture composed of 1000 lb organic base, 790 lb of 66° Bé sulphuric acid, and 2515 lb water. (Approximately 22% H_2SO_4 by wt.) Stirred at 35 r.p.m.

Temperature: 225–230° C (437–446° F).
Duration of tests: 48 hr and 224 hr.

Material.	Corrosion rate, inch per year.	
	48-hr test.	224-hr test.
Monel	0·16	0·19
Nickel	1·44	—
Inconel	1·48	—
Silicon bronze	0·043	0·13
Hastelloy B	0·27	0·49
Hastelloy C	2·01	—
Illium R	*	—
Chemical lead	0·050	0·53
Antimony lead	0·029	0·016
Tellurium lead	0·11	0·036
14·5% silicon cast iron	0·32	0·12

* Destroyed by corrosion. Original thickness 0·031 inch.

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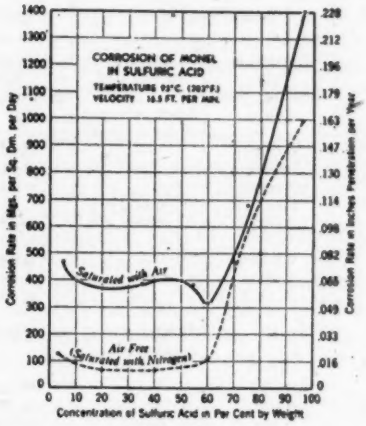


FIG. 29.

Hastelloys, Durimet, LaBour Metal, Illium (Table III), and the high silicon irons. Pioneer Metal, as well as some of the alloys listed, are used in valve parts.

Fuming sulphuric is oxidizing in nature and is resisted well by alloys high in chromium. (See Table XXVII.)

(2) *Hydrochloric Acid.* Hastelloy B is probably the best-known alloy used to resist hydrochloric acid due to the part it played when the method of isomerization employing an HCl atmosphere was introduced during the war. Nickel is extensively used in one of the HCl isomerization processes.

Its resistance is associated with the inhibiting action of the catalyst which is stated to contain antimony chloride. It seems that the process utilizing aluminium chloride as a catalyst requires Hastelloy B or its equivalent for protection, whereas the other process mentioned can make use of nickel

TABLE XXVII.

Tests of Three Metals in Fuming Sulphuric Acid.

Temperature : 188° F (±2° F).
Time : 66½ hr.
Rotation : 16 feet/min for 42 hr, quiet 24½ hr.

Metal.	Penetration, inch per year.
1. 24 chrome–12 nickel	0·008
2. 25 chrome–20 nickel	0·009
3. Mild steel (S.A.E. 1020)	0·118

TABLE XXVIII.

Study of Alloys in Isomerization Units.

Corrosive : Hydrochloric gas and acid.
Process : Isomerization of butane.
Duration : 1050 hours.
Temperature : 240° F average.

Material.	Spool No. 1 (tar).		Spool No. 2 (vapour).	
	Corrosion rate, inch per year (av.).	Pitting during test, inches. Surface (max).	Corrosion rate, inch per year (av.).	Pitting during test, inches. Surface (max).
Monel	0·0261	—	0·0243	0·004
Nickel	0·0095	—	0·0128	0·010
Inconel	0·0106	—	0·0120	0·002
18–8 stainless	—	0·002 *	—	0·008
Type 304	0·0945	0·002 †	0·0500	0·010
18–8 Mo stainless	—	—	—	0·006
Type 316	0·111	—	0·048	0·004
Hastelloy B	0·0004	—	0·0008	—
Silver	0·0479	Perf.	0·065	Entirely corroded
Copper	0·13	Entirely corroded away	0·0438	0·003
85–5–5–5 bronze	0·145	—	0·0580	—
Ni-Resist	0·0525	—	0·0515	—
Mild steel	0·162	0·005 ‡	0·0810	0·002
Cast iron	0·085	—	0·0826	—

* One-half of specimen corroded away.
† One-third of specimen corroded away.
‡ One-eighth of specimen corroded away.

and even Monel for protection. The temperatures, pressures, and cuts of petroleum isomerized vary in the processes and undoubtedly influence the selection of the protecting metal. Table XXVIII gives some results of tests made under isomerization conditions.

It has been previously pointed out that the resistance of Monel to the

hydrochloric acid contained in reflux has dictated its use as the top trays and lining of bubble towers (Table XXIX).

TABLE XXIX.

Results of Tests in Top of Bubble Towers.

Temperature: Crude:	250° F. West Texas.	Approx. 200° F. Michigan.
Metal.	Penetration rate, inch per year.	
Mild steel	Destroyed	0·0500
5% nickel steel	Destroyed	—
18% chrome–8% nickel	Destroyed	0·0254
17 nickel–11 molybdenum–3 chrome	0·0527	—
Monel (69 nickel–29 copper)	0·0031	0·0075
Nickel	0·0057	0·0069
Ni-Resist cast iron	0·0513	0·0131
Cast iron	0·1810	0·0430

(3) *Caustic.* Caustic solutions of various concentrations find nearly as wide employment in petroleum refining as does sulphuric acid. It is used to wash hydrogen sulphide from various cuts, to neutralize acid, and to remove mercaptan sulphur from gasoline. For the last service, higher concentrations of NaOH are used ranging from 50° Bé to molten caustic. The equipment handling the concentrated caustic and the units used to concentrate weak solutions suffer attack if of steel, cast iron, or copper alloys.

Monel is used as tubes of the heaters in caustic regenerators (concentrators) and as the lining of the vessels exposed to caustic attack. For high concentrations, nickel is preferred, and a low carbon variety L nickel is suggested for very high concentrations.

Due to caustic embrittlement of steel in which stresses reside, the storage of high concentration caustic at elevated temperatures, 250° F and above, is done in *riveted* steel tanks. If Monel-clad or nickel-clad steel is used, welding can be applied with satisfactory results. However, stress relieving of the finished vessel would be desirable. For high concentrations and temperatures above 600° F, the cladding on the steel should be L nickel.

The results of some tests made in caustic are reported in Tables XXX to XXXIV.

(4) *Phosphoric Acid.* This acid is used as a catalyst in polymerization of certain components. It is fairly corrosive under certain conditions, notably as a contaminant in condensed water which results from the steam "blow back." Monel is used to line equipment subject to this corrosive condition. Monel, Hastelloy C, and the molybdenum-containing 18–8 alloys such as Type 316 and 317 possess good resistance to phosphoric acid in concentrations up to 35 per cent. Apparently concentration of acid, temperature, and the presence of other materials affect the corrosion rate to such an extent that a general suggestion of a resistant material can rarely be made. Testing by exposing a number of alloys is suggested.

TABLE XXX.

Plant corrosion test in reboiler of regenerator unit used to regenerate caustic solutions used to remove mercaptans from petroleum products. Test specimens located in top part of reboiler directly above heating tubes. Composition of aqueous solution entering tower : 1 to 2% sodium hydroxide, 10% sodium phenolate, 3% sodium sulphide, plus 0·07 mg per 100 cc of the liquid as sodium mercaptides.

Average temperature : 255° F.
Duration of test : 131 days.

Material.	Corrosion rate, inch per year.
Monel	0·001
Nickel	0·024
Inconel	0·0001
70–30 copper nickel	0·025 *
5% Ni steel (S.A.E. 2512)	0·004 *
3% Ni steel (S.A.E. 2315)	0·003 *
Mild steel	0·020 †
Ni-Resist	0·023
Cast iron	0·017

* Pitted to max depth of 0·002 inch during test.
† Pitted to max depth of 0·012 inch during test.

TABLE XXXI.

Plant corrosion test in reboiler of regenerator unit used to regenerate caustic potash solutizer solutions used to remove mercaptans from petroleum products. Composition of solution entering reboiler : 25·5% potassium hydroxide, 37·8% potassium *iso*-butyrate, 5·5% potassium sulphide, 1·9% potassium mercaptides, 2·1% potassium carbonate.

Test 1.—Immersed in boiling liquid at upstream side of overflow weir.
Average temperature : 286° F.
Duration of test : 140 days.
Test 2.—Suspended in vapour at downstream side of overflow weir.
Average temperature : 286° F.
Duration of test : 140 days.

Material.	Corrosion rate, inch per year.	
	Test 1 : Liquid.	Test 2 : Vapour.
Monel	0·003	0·002
Nickel	0·022	0·016
Inconel	0·001	0·002
18–8 stainless (Type 302)	*	0·021
18–8 stainless (Type 304)	*	0·022
70–30 copper-nickel	0·015	0·012
5% Ni steel (S.A.E. 2512)	0·038	0·019
4–6% Cr steel (Type 502)	*	0·017
Mild steel	†	0·012
Ni-Resist	0·046	0·019
Cast iron	0·040	0·014

* Completely destroyed by corrosion during test. Original thickness of test specimens 0·032 inch.
† Completely destroyed by corrosion during test. Original thickness of test specimens 0·062 inch.

TABLE XXXII.

Plant corrosion test in bottom of regenerator tower used to regenerate potassium hydroxide solutizer solutions used to remove mercaptans from petroleum products. Composition of solution entering regenerator tower: 12·5% potassium hydroxide, 19% potassium *iso*butyrate, 28% alkyl phenolate, 0·4% mercaptans, and 0·8% sulphides.

Average temperature: 370° F.
Duration of test: 276 days.

Material.	Corrosion rate, inch per year.
Monel	0·0007
Nickel	0·0010
Inconel	0·0005
18–8 stainless (Type 302)	0·0024
18–8 stainless (Type 304)	0·0023
18–8 Mo stainless (Type 316)	0·0041
70–30 copper-nickel	0·012
Mild steel	0·0023 *
Ni-Resist	0·010
Cast iron	0·006

* Pitted to max depth of 0·004 inch during test.

TABLE XXXIII.

Plant corrosion test in vapour section of regenerator tower used to regenerate a caustic solution used to remove mercaptans from petroleum products. Composition of solution entering tower: 13·2% sodium hydroxide, 0·37% sulphide sulphur, 0·80% mercaptan sulphur.

Average temperature: 300° F.
Duration of test: 55 days.

Material.	Corrosion rate, inch per year.
Monel	0·0016
Nickel	0·0016
Inconel	0·0003
18–8 Mo stainless (Type 316)	0·0030
25–12 Cr–Ni stainless (Type 309)	0·0020
5% Ni steel (S.A.E. 2512)	0·014 *
2% Ni–1% Cu alloy steel	0·017 *
Mild steel	0·033 †
Ni-Resist	0·013

* Some fine stress-corrosion cracks around stamped stencil marks.
† Pitted to max depth of 0·018 inch during test.

(5) *Hydrofluoric Acid.* Hydrofluoric acid was introduced to refineries during the war as a catalyst in isomerization units. Little was known of its behaviour in this service and much had to be found out rapidly. A summary made by the writer [11] in 1944 follows:

"1. Silver is probably the most resistant metal so far tested. The effects of other corrosives present in petroleum products, *e.g.*, sulphur, upon this metal remain to be evaluated; *

"2. Monel is possibly the most satisfactory commercial alloy for use with hydrofluoric acid in both the aqueous and anhydrous state,

* The silver linings were nearly all destroyed in service.

TABLE XXXIV.

Tests in Caustic Soda Vapours and Live Steam.

Process involved : Caustic regeneration.
Location of specimens : In caustic vapour.
Temperature : 300° F.
Agitation : Vapour flow.
Duration of Test : 55 days.
Corrosive Reagent : Caustic solution.

Sp. gr. 1·175.	
Free caustic (NaOH)	13·2% by weight
Total alkalinity	15·9% ,,
Sulphide sulphur	0·37% ,,
Mercaptan sulphur	0·80% ,,

Metal.	Corrosion rate, inch per year.	Pitting.
Monel	0·0016	—
Nickel	0·0016	—
Inconel	0·00034	—
25 Cr-12 Ni (Type 309)	0·0015	—
16 Cr, 13 Ni, 3 Mo (Type 316)	0·0030	—
Mild steel	0·0328	0·018 (edge attack)
5% nickel steel	0·0142	Fine cracks around stencil marks
Ni-Resist cast iron	0·0132	—
Grey cast iron	Specimens lost	—

TABLE XXXV.

Monel Corrosion Tests in Hydrofluoric Acid.

Material.	Acid conc., %.	Temp., ° F.	Agitator, gas.	Time, days.	Area,* dm^2.	Corrosion rates. Mdd.†	Corrosion rates. Ipy.‡
Air-free tests. Nitrogen agitation rate = 100 cc/min.							
Monel (wrought) (approx. 69% nickel; 29% copper)	25	86	nitrogen	6	0·50	1·0	0·0002
	25	176	nitrogen	6	0·50	14·5	0·0024
	50	86	nitrogen	6	0·50	0·4	0·0001
	50	176	nitrogen	6	0·50	3·6	0·0006
Monel (cast)	25	86	nitrogen	6	0·13	3·5	0·0006
	25	176	nitrogen	6	0·13	8·3	0·0014
	50	86	nitrogen	6	0·13	2·8	0·0005
	50	176	nitrogen	6	0·13	13·5	0·0022
S-Monel (cast) (approx. 4% silicon)	25	86	nitrogen	6	0·30	1·5	0·0002
	25	176	nitrogen	6	0·30	1·1	0·0002
	50	86	nitrogen	6	0·30	2·3	0·0003
	50	176	nitrogen	6	0·30	1·21	0·0020
Air saturated *v.* air-free tests. Air agitation rate = 300 cc/min. Nitrogen agitation rate = 100 cc/min.							
Monel (wrought)	25	86	air	1	0·50	230·0	0·0380
	25	86	nitrogen	6	0·50	1·0	0·0002
	25	176	air	1	0·50	67·0	0·0110
	25	176	nitrogen	6	0·50	14·5	0·0024
	50	86	air	1	0·50	48·7	0·0079
	50	86	nitrogen	6	0·50	0·4	0·0006
	50	176	air	1	0·50	241·0	0·0100
	50	176	nitrogen	6	0·50	3·6	0·0006

* dm^2 = square decimeter.
† Mdd. = milligrams per sq. decimeter per day.
‡ Ipy. = inches penetration per year.

provided oxygen is absent. The effect of oxygen is shown [Table XXXV of this paper] in the section dealing with 'Air-Saturated *v.* Air-Free Tests';

"3. Copper is very resistant to aqueous HF solutions, but is vigorously attacked by anhydrous HF. Other elements in the oil may attack copper;

"4. Steel is vigorously attacked at temperatures above about 150° F;

"5. 70/30 copper nickel alloy has made a good showing in laboratory tests in both aqueous and anhydrous HF acid."

The above information appears pertinent to-day. Monel is the most widely used alloy in these HF units to resist attack by the acid.

(6) *Naphthenic Acids.* Naphthenic acids are quite corrosive at elevated temperatures. The results of some tests are reported in Table XXXVI.

TABLE XXXVI.

Results of Some Studies of Corrosion by Naphthenic Acids.

Temperature: 550° F.
Location: column of vacuum unit.

Metal.	Penetration, inch per year.
Mild steel	0·0163
18 chrome–8 nickel	0·0236
18 chrome–8 nickel–3 molybdenum	0·0002 *
16 chrome–13 nickel–3 molybdenum	0·0009 *
Inconel (80 nickel–13 chrome)	0·0007 *
Monel (69 nickel–20 copper)	0·0012
Nickel	0·0006
Ni-Resist (cast iron)	0·0109
Cast iron	0·0080

* Three applicable metals. Possible sulphur attack (above 500° F) precludes Monel or nickel. Monel in use at temperatures below 500° F.

Inconel (approximately 79 per cent Ni, 14 per cent chromium) and the molybdenum-containing 18–8 type alloys are quite resistant to naphthenic acid attack and are used. Fig. 31 shows some Inconel exchangers in service where attack from these acids was a source of corrosion.

Monel and nickel are useful at low temperatures to resist attack by naphthenics. Their use in refineries is limited to temperatures below 500° F for fear of sulphur attack.

The surprising feature in the data associated with Table XXXVI was the low order of resistance of the 18–8 alloy. This low resistance was amply checked and proven during a series of tests.

(7) *Solvents.* (*a*) Furfural. Furfural, after some service as a solvent, becomes corrosive. Monel is extensively used to combat corrosion from this solvent. Where the metal temperature exceeds 500° F, the 18–8 stainless steels are suggested (Table XXXVII).

(*b*) Phenol. Phenol is used as a solvent in the extraction of lubricants. 18–8 heating tubes and liners are used to combat its corrosive qualities.

(*c*) Ethanolamine. The *mono-*, *di-*, and *tri-* forms of ethanolamines are used as solvents for carbon dioxide and hydrogen sulphide. The 18–8

stainless steels are used in locations where corrosion occurs. The corrosion of steel by these solvents is associated with high local velocity and the presence of oxygen, sulphur, and other factors. These solvents are very corrosive to copper-rich alloys and such alloys must be omitted from their presence. Monel (2/3 nickel, 1/3 copper) is quite resistant to these solvents.

(*d*) Chlorinated Solvents. Nickel and Monel are widely used in connexion with chlorinated solvents both to resist the attack that occurs on

TABLE XXXVII.

Results of Tests in Furfural Solution.

Process involved : Recovery of furfural used in refining lubricating oils.
Location of Specimen : Downpour between bubble trays.
Temperature : 460° F max, 450° F average.
Duration of test : 121 days.
Aeration : None.
Agitation : Due to flow of liquids.

Metal.	Corrosion rate, inch per year.	Pitting, inches.
Monel	0·00004	—
Nickel	0·00003	—
Inconel	No attack	—
Type 302 stainless	No attack	—
Type 316 stainless	0·00001	—
Chemical lead	0·0026	Perforated
13% Cr stainless	0·0014	0·017
Aluminium, 2S	0·00016	—
Mild steel	0·01112	Perforated
Ni Resist cast iron	No attack	—
Grey cast iron	0·00004	—

steel from the break-down product of these solvents and to resist the tendency to break down.

Nickel is the material most generally used in connexion with chlorination of hydrocarbons.

Elevated Temperatures (500° *to* 1300° F).

(a) *General.*

Within the temperature range of 500° to 1300° F some changes are noted, compared with lower levels in the type of corrosion encountered and in the behaviour of metals.

As far as corrosion is concerned, oxidation of the metal becomes a factor at the upper temperature levels. Sulphur attack becomes a prominent cause of metal corrosion and naphthenic acids attack certain metals with vigour.

(b) *Stress Rupture.*

The mechanical properties of metals undergo changes as the temperature increases. Above about 750° F, it is usual to consider the metal as becoming more plastic in its behaviour under stress and increasingly less elastic. Above the 750° F temperature level, interest is felt in the creep tendency (*i.e.*, tendency to continuously elongate in the direction of major stress) of a metal.

In the past, considerable work has been done in measuring creep rates

of metals and these data have been used in the design of refinery equipment. The creep tests are an unnecessary refinement for most refinery equipment, and stress-rupture data are being relied upon to an increasingly great extent for present design. The stress to rupture data define the limit of stress-carrying ability in a manner not defined by creep–stress data and hence serve as a warning in design of equipment that can normally suffer marked deformation without sacrifice of usefulness. There is apparently an empirical relationship between the creep- and stress-rupture properties, and this has been worked out for many of the commonly used metals in a refinery. This relationship is considered useful by many engineers. Table XXXVIII gives some stress-rupture values for a number of materials used in petroleum refining equipment, especially tubing.

(c) *Corrosion.*

Sulphur attack, which is quite a factor within this temperature level, is resisted by the presence of chromium in the alloy. The effects of chromium

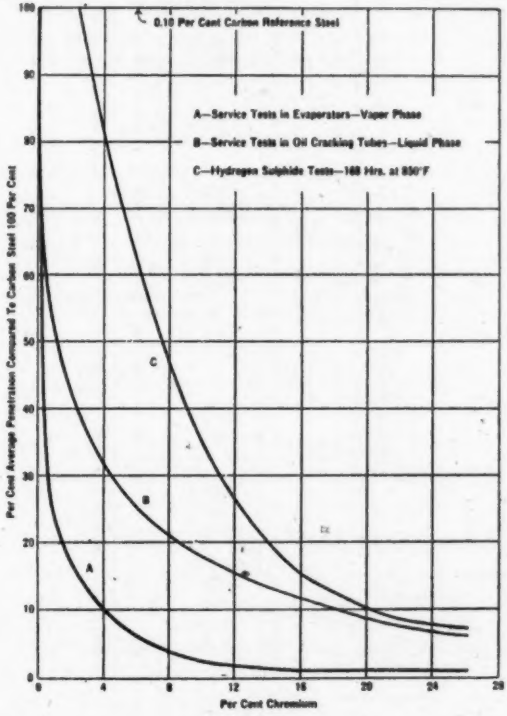


FIG. 30.

CHROMIUM VS SULPHUR ATTACK.

in reducing sulphur attack is quite marked for the first few per cent of chromium (Fig. 30), and less marked with greater additions, though benefit

TABLE XXXVIII.

Stress–Rupture Data for some Heating Coil Tube Steels.

(Stress to produce rupture in time, at temperatures given—pounds per square inch.)

Temperature, ° F.	950.		1,000.		1,100.		1,200.		1,300.		1,500.		Heat treatment.	BHN.
Time to rupture, hrs.	100,000.	10,000.	100,000.	10,000.	100,000.	10,000.	100,000.	10,000.	100,000.	10,000.	100,000.	10,000.		
Steel Designation.														
0·50 Mo steel	10,500	19,500	6,800	12,400	2,150	5,000	1,800	3,100	525	1,100	—	—	Hot Rolled	137
2% Cr–0·5 Mo	—	—	10,500	15,000	6,400	9,000	3,000	4,600	1,100	1,900	—	—	Annealed	163
4–6% Cr–0·5 Mo	—	—	14,500	17,000	6,700	9,000	3,000	4,700	1,300	2,100	105	280	Annealed	163
9% Cr–1·0 Mo	—	—	—	—	11,800	14,500	4,600	6,200	1,600	2,500	420	700	Annealed or normal tempered	179
18% Cr–8% Ni (304)	—	—	—	—	—	—	7,200	10,000	3,700	5,800	1,700	2,600	Quenched or normalized	200
25% Cr–20% Ni (310)	—	—	21,000	26,000	16,000	20,000	7,800	11,500	4,400	7,000	1,600	2,700	Quenched	200

Data: *Digest of Steels for High Temperature Service*, 5th Edition, 1946. The Timken Roller Bearing Company, Canton, Ohio, U.S.A.

is received from the greater additions that often justify its use. The benefits of the first additions of chromium are taken advantage of by the extensive use of 4 to 6 per cent chromium alloy steels. An addition of ½ per cent of molybdenum to this alloy is made to correct its tendency to become temper brittle. The molybdenum also confers better creep-resisting properties upon the alloy. The chromium content is increased or decreased, depending upon the severity of sulphur attack. Molybdenum content increases slightly with increase of chromium up to about 10 per cent chromium, ranging from 0·5 per cent in the 4 to 6 per cent chromium alloys to 1·0 per cent or more in the higher chromium steels. Where more than 14 per cent chromium is indicated the tendency is to use the austenitic alloys such as 18–8. The nickel serves to prevent brittleness. It also enhances the creep strength.

The high chromium alloys are widely used as liners, also caps and trays to combat sulphur attack. Reactors, high temperature separators, and bottoms of bubble towers are often lined with 11 to 14 per cent chrome, or with 18–8 stainless steel (usually stabilized). Strip lining appears favoured for high temperature service and the matter of lining has been discussed extensively in the literature. A summary is provided in the following :

Lining With Stainless Steel (Strip Lining).

" Strip lining has been found most satisfactory for use at elevated temperatures. The thickness of metal should be not less than 12 gauge (0·1093 inch U.S. Standard), the width of strip as suggested by a bulletin of The U.S. Steel Corp.[16] follows :

Operating temperatures, ° F.	Width of strips, inch.
950 to 1000	3
850 to 950	3½
750 to 850	4
Up to 750	4½

" For ease in handling during fitting-up, and to obtain at least an occasional transverse weld, the lengths are generally held to a maximum of 5 feet when applying them vertically."

Other important points made in this bulletin are abstracted as follows :

The method calling for solid welding of one edge of the first strip to the steel shell, thoroughly cleaning this weld bead, inspecting it, re-welding if and, where necessary, firmly butting the next strip against this completed weld bead, tacking it in place, solid welding the opposite edge, etc., is strongly favoured.

Before attempting to apply a stainless steel liner to a refinery vessel, it is essential that the interior surface of the vessel be *thoroughly* cleaned. This generally is accomplished best by a hard blasting with a sharp sand or steel grit.

If a stainless steel liner is to be applied to a vessel which previously had been metallized with aluminium, it will be essential to remove

all of the aluminium and the possible aluminium–iron alloy from the surface where welding is to be performed.

It is suggested that sufficient care and time be taken in fitting the liner sheets or strips to assure that the stainless steel is snugly against the steel shell at the edges and around the periphery of the plug-weld holes.

All of the welding on the stainless steel liners (excepting, of course, resistance welding in the case of spot-welded liners) should be done by the metallic arc using reversed polarity and a coated rod. Coated rods of 18–8, Type No. 304; 25–12, Type No. 309; and 25–20, Type No. 310 have been used with satisfaction. It is believed, however, that either the 25–12 or the 25–20 rods are to be preferred to the 304 (18–8), inasmuch as there may be an appreciable amount of dilution of the weld bead with iron when welding to the steel shell.

Both the $\frac{1}{8}$-inch diameter and the $\frac{5}{32}$-inch diameter coated welding rods have been widely used for the field application of stainless steel liners.

It is important, however, that the amount of heat used should be held closely to the *minimum necessary to obtain the desired penetration.* Generally, the heat used *should not be greater than* 130 amperes when using $\frac{5}{32}$-inch diameter rod and no greater than 95 amperes when using the $\frac{1}{8}$-inch diameter rod.

Many new vessels are formed from steel clad with stainless by one of the processes referred to previously, namely, "Cladding," "Pluramelt," "Smithlining," "Croloy" bonding, etc., sponsored respectively by Lukens, Kellogg, A. O. Smith, and Babcock and Wilcox. These linings have been generally reported upon favourably. As has been pointed out before, the top of bubble towers are often cooled by return reflux and attack by mineral acids, such as hydrochloric, takes place. For these top locations, Monel is more satisfactory and is widely used.

While the high chromium alloys (11 per cent chromium and above) can resist sulphur attack in an excellent manner, they are subject to naphthenic acid attack (Table XXXVI). To resist this organic acid at elevated temperatures, resort is made to the molybdenum-containing alloys such as 18 per cent chromium–13 per cent nickel–2 to 3 per cent molybdenum (Types 316 and 317), or to Inconel (79 per cent nickel–13 per cent chromium–6 per cent iron). An installation of Inconel heat exchangers has been in operation for a number of years (Fig. 31) where attack from naphthenic acids had proved troublesome. On the west coast of the United States some towers exposed to naphthenic acid attack are lined with both Inconel and Type 316 as part of a general study. It will be noted from Table XXXV that both Monel and nickel resisted the naphthenic acid attack, but their use was not considered, as the temperature of operation exceeded 500° F which has been set as the upper limit for Monel or nickel in a refinery. This is based on the possibility of sulphur attack above this temperature limit.

(d) *Tubes—Fired Coils.*

In the matter of tubes for fired coils, nothing to date has equalled the

resistance of the 18 per cent chromium–8 per cent nickel alloy to both sulphur and to operating stresses (Table XXXIX). Tubes of the alloy are

TABLE XXXIX.

Some High-temperature Properties of Inconel.[17]

Temperature, ° F.	Creep strength for secondary creep rate of 1·0% elongation per 10,000 hr., p.s.i.		Fatigue strength for 10^8 cycles of completely reversed stress, p.s.i.	Charpy impact strength, ft-lb.
	Hot-rolled condition.	Annealed * condition.	Annealed condition.	Annealed condition.
Room	—	—	51,500	180
800	—	—	47,500	187
900	39,000	—	—	—
1,000	22,000	—	38,000	160
1,100	11,000	—	—	—
1,200	5,500 †	5,500	30,000	160
1,300	3,000 †	4,000	—	—
1,400	1,800 †	3,000	15,500	154
1,500	1,100 †	2,000	—	—
1,600	710	1,500	10,000	—
1,700	470	1,100	—	—
1,800	330	640	—	—

* Two hr. at 2,000° F followed by quenching in water.
† By extrapolation.

reported to have been in service for 70,000 to 100,000 hours, during which time high sulphur feed stocks from west Texas and other crudes passed through them. The large crystal size of this austenitic material is considered to account for its high creep and stress-rupture resistance. The expense of the tubes limits them to last consideration in selecting alloy tubes. The 4 to 6 per cent chromium and the 9 per cent chromium alloys, with suitable molybdenum addition, do an excellent job in most locations in refinery fired coils.

An interesting insight into the behaviour of 18–8 tubes and the method by which these tubes are protected by a film of sulphur or oxygen was provided by the failure in short order of 18–8 tubes in a unit cracking naphtha at high temperatures (1310 to 1325° F).[18] When sulphur (0·05 to 0·5 per cent) was added to the feed stock or (0·06 to 0·4 per cent) water the corrosion was stopped, indicating a film-forming material, sulphur or oxygen, must be present to make the chromium effective in preventing corrosion. Coking appeared also to be suppressed by the addition of sulphur or water.

(e) *Pumps—Hot Oil.*

Hot-oil pumps are a very special case. For centrifugal pumps the impellers, the shaft, and sleeves are of various grades of stainless steel. Stellite is widely employed where a wearing face is needed.

In reciprocating pumps, the blocks or liners in the blocks are often of 4 to 6 per cent chromium, 0·5 per cent molybdenum alloy. The plunger is often of heat-treated complex alloy steel or may be lined with a corrosion-

and packing-resistant liner. The plungers are generally water cooled. The pump valves are preferably of a high carbon, high chromium alloy, as 1·0 to 1·5 per cent carbon, 17 to 19 per cent chromium, fully hardened by heat treatment.

(f) *Valves.*

Valves of 4 to 6 per cent chromium alloy trimmed with stainless steel are used in hot lines. Fittings often are of 4 to 6 per cent chromium or some higher chromium alloy with the usual molybdenum content.

It will be observed that the temperature region of 500° to 1300° F is one where the chromium-containing alloys, such as the stainless steels, are used to combat sulphur attack. Where the attack is from naphthenic acids, the choice is limited to Type 316 or 317 stainless steel (an 18–8 with molybdenum 2 to 4 per cent) or Inconel (approximately 79 per cent nickel-13 per cent chromium alloy). These alloys are widely useful in a petroleum refinery, as will be noted from corrosion study results, and can be relied upon if their cost can be justified. The choice between these two alloys is often based on availability of certain forms as seamless tubing or upon some differing physical property such as the lower coefficient of thermal expansion of Inconel.

Within the temperature level 500° to 1300° F, a powdered catalyst is used that presents problems of abrasion. Little has been published in connexion with this problem, but from current reports it seems that carbon steel and grey cast iron offer as good resistance as can be obtained from any alloy. Studies are being conducted and a report upon this interesting subject may be forthcoming in the near future.

High-Temperature Region (1300° *to* 2000° F).

(a) *General.*

The region of temperature above 1300° F makes strenuous demands upon the oxidation resistance and the resistance to creep of alloys. Fortunately, the combinations of chromium and nickel (totalling above 36 per cent of the composition of the alloy) that give satisfactory resistance to oxidation at high temperature also provide the best load-carrying qualities in the alloys.

(b) *Corrosion.*

Sulphur is an enemy of the heat-resisting alloys and can cause destruction. It is most harmful in the form of hydrogen sulphide, and least in the form of sulphur dioxide. This necessitates a burner that will ensure combustion being completed before the gases strike the hot alloys. An excess of air will be of little avail if mixing is poor, as hydrogen sulphide may strike a hot surface or unburned hydrocarbons, such as methane, may react to form hydrogen sulphide from sulphur dioxide.

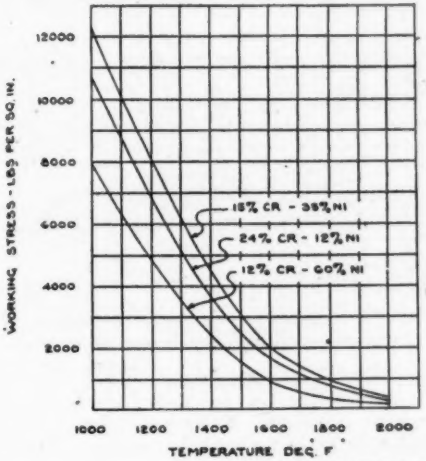
Caustic alkalies are most harmful, and when scrubbing of gases is applied to remove hydrogen sulphide, " carry-over " must be avoided.

Vanadium oxide, resulting from burning of bottoms from some crudes,

such as Venezuelan, are reported as harmful to heat-resisting alloys. This matter is being studied at the present time. The first indication that heat-resisting alloys in which nickel predominates such as Inconel (79 per cent nickel–13 per cent chromium) and 35–15 (35 per cent nickel–15 per cent chromium) resist well the vanadium oxide has not been confirmed, and some doubt of its validity exists.

(c) *High-Temperature Strength.*

Cast heat-resisting alloys are extensively used as tube supports in fired coils. The 28 per cent chromium, 12 per cent nickel has established itself as the most popular in the United States. It seems to resist oxygen, sulphur compounds, chiefly sulphur dioxide, and other attacking agents



[*The Ohio Steel Foundry Co.*

FIG. 32.

WORKING STRESS FOR SOME CAST HEAT-RESISTING ALLOYS.

in a most satisfactory manner. The castings as a rule are massive, and so provide sufficient strength for normal conditions over a period of years, or for such abnormal conditions, as a fire, over a period of time that will permit regaining control. Fig. 32 gives some representative values for the load-carrying abilities of several popular compositions of heat-resisting castings.

An extending use of heat-resisting alloys in petroleum refineries is noted as high-temperature reactions, such as forming of hydrogen from methane; cracking at high temperatures and others are increasingly carried out. The equipment involves tubes and other wrought forms of heat-resisting alloys. The 25 per cent chromium, 20 per cent nickel alloy, Type 310, is one of the most popular in refinery service and finds applications as tubing, headers, manifolds, etc. Much study of its properties has been made and is available in numerous reports.[14, 15, 16] Stress-rupture data for the

25 per cent chromium–20 per cent nickel alloy are provided in Fig. 33.[14] The curve for 1800° F (a much used temperature level), responds to the formula : *

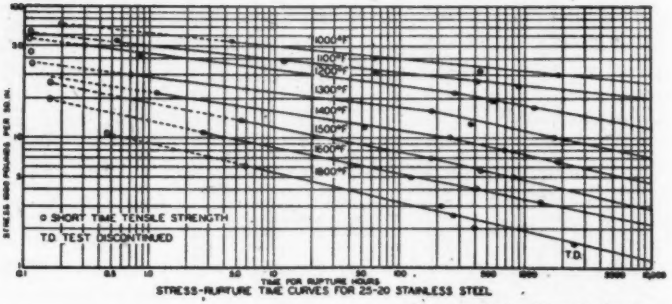
where S = Stress, p.s.i. T = Time, hrs. $S = \dfrac{9200}{(T)^{\cdot 227}}$

or

$$\text{Log}_{10}\ \text{Stress} = 3{\cdot}963 - 0{\cdot}227\ \text{Log}_{10}\ \text{time in hours},$$

according to this writer. This formula may be used for extrapolating if one feels warranted in exceeding the 2500 hours reported for the most extended test.

Inconel (approximately 79 per cent nickel, 13 per cent chromium) has been used as a tubing in the high-temperature service of cracking and



[*Courtesy Timken Roller Bearing Co.*

FIG. 33.

treating of petroleum vapours. Extruded tubes of this composition, 3 inches and 4 inches in diameter with $\frac{1}{4}$ inch and $\frac{3}{8}$ inch walls, are being tested at the present time in connexion with some high-temperature petroleum operations. The oxidation resistance of this alloy at 1800° F appears to be excellent. Its high nickel content gives hopes it will resist carburization better than the alloys in which chromium predominates. The creep strength of Inconel is reported in Table XXXVIII[17] and compares favourably with other alloys suitable for use at high temperatures.

The values presented here for the stress-rupture strength of 25–20 alloy, and the higher value of creep strength of Inconel are from specimens quenched from 2000° to 2100° F. The benefits of this quench are obvious, its mechanism somewhat obscure, and its duration in time unknown. It is assumed an element or compound is put into solution and left there by the rapid quench. Whether or not a precipitation over a period of time at elevated temperatures is to be expected remains to be determined. The tendency is to use the quench and to design on the high strength values so obtained.

* In general, the formulæ appear to be

$$s = \frac{\text{constant}}{(\text{time})^{a}} \quad \text{where} \quad \begin{matrix} \text{const.} = \text{stress to fail in 1 hour.} \\ a = \text{measured slope.} \end{matrix}$$

A chromium (28 per cent) alloy was used in tube form during the war for some high-temperature reactions. This alloy has excellent oxidation resistance, but is much weaker than the austenitic heat-resisting alloys. Its use was dictated, in one case, by the tendency of nickel-containing alloys to deposit nickel over the catalyst, thus changing the reaction to one not desired. The nickel appeared to be deposited as if from a carbonyl which may have formed during a starting-up, or a shutting-down period.

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[9] "High Properties at Low Temperatures," by W. A. Mudge. *Inco Magazine*, Vol. 19, No. 1, The International Nickel Company.

[10] "Notch-Bar Impact Properties of Some Nickel Steels After One Year Exposure to Liquid Nitrogen," by T. N. Armstrong and A. J. Miller, D. and R. Div., The International Nickel Company. (Paper before the Conference of the Petroleum Committee, A.S.M.E. in Tulsa, Oklahoma, 1946.)

[11] "Corrosion in Petroleum Refineries," by B. B. Morton. *The Petroleum Engineer*; May 1944.

[12] "Application of Nickel, Monel and Inconel Lining in Existing Steel Structures." *Mechanical Letter*, No. 8, Technical Service Section, D and R Div., The International Nickel Co.

[13] Specification K-6 covering Ni-Resist cast iron, The International Nickel Company.

[14] "Digest of Steels for High-Temperature Service," Timken Roller Bearing Co., Canton, Ohio.

[15] "Technical Bulletin No. 6-C," The Babcock and Wilcox Tube Co., Beaver Falls, Pennsylvania.

[16] "U.S. Stainless and Heat-Resisting Steels," U.S. Steel Corporation and Subsidiaries.

[17] "Some Engineering Properties of Nickel and High Nickel Alloys," by B. B. Betty and W. A. Mudge. *Mechanical Engineer*, pp. 123–129, February 1945.

[18] "Corrosion of 18–8 Alloy Furnace Tubes in High-Temperature Vapour Phase Cracking Service," by E. A. Camp, Cecil Phillips, and Lewis Cross. *Corrosion* (Official Journal of National Association of Corrosion Engineers), Vol. No. 2, September 1945.

Discussion.

The Chairman (Professor F. H. Garner): We are fortunate in having this paper for the first meeting of the session, since it covers three out of four of the principal branches of the industry. It was mentioned, in connexion with the gas lift apparatus, that provision is made to modify the metal used in the various parts so as to give varying types of resistance. It does seem that in all this work the aim is to use the appropriate metals so that the apparatus as a whole will last for a given length of time. This

applies, I think, to all petroleum equipment in general, to ensure that the equipment as a whole will last for the required period between overhauls; I suppose the ideal would be that it should last until the time of obsolescence. It is rather reminiscent of "The Deacon's Masterpiece or The Wonderful One-Hoss Shay," by Oliver Wendell Holmes, in which the weakest part was made as strong as the rest with a greatly prolonged life of the shay.

I should like to ask Mr Burling-Smith whether he can make any general statement on the question as to how metals such as stainless steel and Monel compare, from the economic point of view, with the steel which they replace, taking into account, naturally, the original capital cost and the extra length of service obtained?

MR BURLING-SMITH: The installation and use of the Monel or stainless steel will involve an initial cost somewhat higher than that of mild steel and the relative economy would depend upon corrosive conditions obtaining in each individual installation.

DR F. MORTON: There are two points on which I should like to comment. The first concerns the detection of corrosion in the operating unit. Have any methods been developed for the detection of corrosion (*a*) *in situ*, and (*b*) for the examination of deposits to ascertain if these are due to corrosion?

Secondly, I was extremely interested in the account of the lining of a fractionating column with two different corrosion-resisting linings for different conditions. However, the actual plate level to which the corrosive reflux descends or the corrosive bottoms ascend will depend upon the operating conditions. I presume that adequate safeguards are provided against unusual conditions or faulty operation? I am reminded of an operator of a fractionating column handling a non-corrosive charge. Both overhead and bottoms products were non-corrosive and in the operation in question no side streams were removed. A very small quantity of a corrosive constituent (acetic acid) had escaped detection in the charge but gradually accumulated in the middle of the tower. Its presence was first detected by a falling off of efficiency due to the disappearance of the middle section of plates.

MR BURLING-SMITH: I think Mr Morton has covered, in his paper, the second point that you raise. He appreciates the difficulty of assessing just where the Monel lining at the top should change to the stainless steel lining at the bottom and recommends the installation of test samples in the critical area in which the corrosive attack changes its character.

With regard to your first enquiry, I presume you are referring to corrosion possibly occurring inside a tube where it cannot be visually inspected. I can only suggest the use of an introscope for internal visual examination and after removal of any deposit a critical examination for corrosion and particularly pitting, which is of course one of the most dangerous types of corrosion.

If any deposit was bottomed you should be able to assess whether corrosion had occurred and certainly serious pitting should be observed very readily.

This is the only method I can suggest for examination of corrosion of

equipment *in situ* where normal visual examination or the taking of samples for closer examination is not possible.

MR E. THORNTON : Could you give any indication of how far the modern techniques maintain the linings, and whether trouble is experienced with the welds or with small leak spots? In the case of any lining, whether enamel, or lead, or stainless steel, you rely on a perfect lining. Do the modern techniques enable you to make a reasonable guess that a lining will stay, or what is the experience to-day with regard to the putting on of the linings and their lasting qualities?

MR BURLING-SMITH : Again that is a matter which is covered very adequately in the paper, in that Mr Morton has reprinted the instructional letter issued to the petroleum industry, making full recommendations as to how the two forms of welding " Plug " and " Strip " should be carried out.

He refers specifically to the fact you have just mentioned—that in the early days a considerable amount of trouble was encountered due to leaks at the welds, particularly plug welds.

I think if one attempted to summarize briefly the recommendations which have been laid down they are that one should use a high alloy welding rod, preferably a 25/20 chromium-nickel when lining with stainless steel or Monel rod when putting on a Monel lining, paying particular attention to factors of welding technique such as precleaning, current conditions, and speed of welding, so that the operator does not undercut or get too much iron dilution in the weld deposit. The application of a final pressure test is also recommended.

On the question of service life of such linings applied by modern technique, I cannot give factual data. I will, however, endeavour to obtain typical life cases from Mr Morton.

DR R. F. GOLDSTEIN : May I, as a mere chemist, congratulate Mr Burling-Smith and Mr Morton for having given us so very much information. The paper is an admirable effort, quite invaluable to anyone who, like myself, is concerned with the design and building of plants which have to deal with chemical materials.

I should like to put some questions. Can Mr Burling-Smith say whether any trouble is experienced with nickel-clad and stainless steel-clad steels in respect of the differential thermal expansion of the steel and of the cladding materials?

Next, is there any change in the corrosion resistance of austenitic steels due to surface change to the ferritic form brought about by the mechanical working, such as drawing, turning, and welding, which is necessary in the fabrication of chemical plant?

Towards the end of the paper the behaviour of alloy steels at very high temperature is discussed. Mr Morton refers to the peculiar behaviour of certain nickel-containing steels at 800° C, which he suggests is due to the formation of nickel/carbonyl and the deposition of nickel in other parts of the apparatus, the nickel then giving an undesirable catalytic effect. Many of us are familiar with the behaviour of very highly resistant steels in leading to deposition and coking at a temperature of 700° C and above,

which we have attributed to nickel in the steel bringing about decomposition of methane to carbon and hydrogen. Can Mr Burling-Smith say anything about this suggested nickel carbonyl? The ordinary nickel carbonyl we know decomposes at atmospheric pressure at about 150° C, and I should expect it to have an insignificant existence at 800° C or above.

Lastly, how do the high-chromium–nickel steels, which are used in the petroleum industry for very high temperature conditions, compare with the nickel-free steels which have been developed in Germany and America and used in conditions where even 25 per cent chromium–nickel steels are desirable, for example, in the manufacture of ketene from acetone or from acetic acid, where a certain amount of carbon monoxide is produced as a by-product? In America they use high-chromium steels containing nitrogen. In Germany they use "Sicromal 12," having 23 per cent chromium, 1 per cent silicon, and 2·5 per cent aluminium. I should be very glad if Mr Burling-Smith could give any information concerning the behaviour of these types of high-chromium nickel-free steels compared with the 25/20 chromium–nickel steel, from the point of view of freedom from undesirable catalytic reactions, and from the point of view of fabrication, construction, and maintenance.

MR BURLING-SMITH : I must confess that with regard to the special catalytic reactions to which Dr Goldstein refers, I cannot add anything. I will, however, ask Mr Morton to add to the brief reference he has given.

With regard to the relative merits of the 25/20 chromium nickel steel and the high-chromium nickel-free steel grain refined, I think the matter can be summed up by asking what you want from the steel. If you want a combination of heat resistance, corrosion resistance, and strength at elevated temperature, you have to use a steel containing both chromium and nickel. If you will be satisfied with high corrosion resistance, but nothing like the same order to elevated temperature strength, the 28/30 chromium steel will be admirable, but will certainly not give the elevated temperature properties of the chromium nickel steel. In addition it is a much more difficult steel to weld and more liable to pick up carbon, which with time will tend to embrittle the whole component.

On the effect on the corrosive resistance of the 18/8 steels of cold working, the effect is definitely to lower corrosion resistance. With high cold working there is the formation of a pseudo martensite on the surface and with light cold working there is some slight diminution in corrosion resistance. To some extent this effect can be compensated for by the selection of an austenitic steel with increasing nickel, which stabilizes the austenitic phase, so that at cold working there is less tendency to form a pseudo martensite.

The drop in corrosion resistance with cold work can, however, be eliminated by subsequent high temperature annealing heat treatment where the application of this is practicable. Where maximum corrosion resistance and workability is desired, we would recommend an 18 per cent chromium steel, containing 10 or 12 per cent nickel.

With regard to the thermal expansion differential as between the steel and the cladding material in an homogenous clad material, *i.e.*, where you have essentially a pressure weld over the whole surface as produced by pack

rod and where appreciable operating temperature fluctuations occur, if you cannot design to compensate for the definite panting or bowing which will occur, due to differential expansion at elevated temperatures, I could imagine you might easily experience trouble.

The welded type of clad material, particularly the plug welded or resistance welded type, seem somewhat better able to withstand panting and thermal expansion trouble. In some cases a layer of nickel is interposed between the steel backing and the stainless steel facing, and I believe one of its functions is to help to balance the expansion differential by the insertion of a buffer layer having an intermediate coefficient of expansion between the steel backing and the stainless steel.

The coefficient of expansion of ordinary steel is about 10, that of nickel about 14, and that of stainless steel about 18.

Mr W. M. Catchpole: In the part of the paper headed "Condensers" the author states that the practice of introducing ammonia, caustic or some other base into the gases entering the condenser "invariably leads to the destruction of the tubing since the effort to maintain a neutral water leaving the condenser represents a task beyond the ability of the operators." It is my experience that, provided the plant is large enough and there is sufficient water going over to carry away the ammonia at a reasonable pH value, that control of pH is not beyond the ability of the operators. We use tinned Admiralty tubes, and certainly we have not had trouble due to ammonia, nor do we find copper in the condensate.

We have tried a chemical rather than a metallurgical method of combating corrosion in a distillation unit, and that has led to a very nice problem. We introduce aqueous caustic soda solution into topped crude at about 450° F, flashing off the water, and thereby producing a suspension of caustic in oil. This material is injected to the crude feed to the tower but has proved extremely difficult to pump, being abrasive as well as corrosive. Stainless steel (an 18/8 + 1 per cent tungsten alloy) impellers were used, but this material was soon given up because of destruction by cracking of the impellers. The impellers disintegrated rather than eroded or corroded. This cracking was found not to follow any grain boundary and to be transcrystalline. The trouble was ascribed eventually by our metallurgist to incorrect heat treatment, but it might be one of those cases, as suggested by Mr Morton, where there is no film-forming element present.

However, because of this cracking stainless steel was condemned and "Mechanite" used. The life of the latter is very short, a matter of a few months only; it is of interest to note that one refinery was able to fit impellers of "Ni-resist" cast iron on this duty. These gave about four times the length of service of Mechanite. We are now turning our attention to stainless steel again, and can you say what would be considered the best type of steel for such a duty?

Mr Burling-Smith: I would like to see or hear more about the failure which occurred in the stainless steel. If there was inter-granular corrosion I would say that the theory of incorrect heat treatment is probably valid and that the trouble was due to inter-granular corrosion or weld decay, rather than to any inherent inadequate corrosion resistance.

I should think that a normal 18/8-type steel, stabilized with titanium or columbium would be worth a retest, but if we are to make a firm recommendation concerning an application giving so much trouble, I should be inclined to favour molybdenum-bearing stainless steel known as 18/10/3, *i.e.*, 18 per cent chromium, 10 per cent nickel, and 3 per cent molybdenum.

MR JOHN HENRY : With regard to the selection of steel for sucker-rods and bearing in mind the varying nature of the corrosive fluids, is there any possibility of the development of a standard procedure in the conduct of the corrosion-fatigue test which would assist the field man in his appraisal of the relative values of the various alloys offered to him in the form of sucker-rods or other sub-surface equipment? I assume that, except in special circumstances, it would be impracticable to conduct tests for individual cases because of the length of time required to carry out the tests and to obtain samples of well fluids, which are quite often of an unstable character.

Secondly, I was wondering whether we could have an air endurance limit for the K-Monel sucker-rod steel described in Table VIII.

MR BURLING-SMITH : Your first question is certainly a difficult one. Corrosion testing can be such a variable matter when you are trying to represent in laboratory tests the actual corrosive conditions encountered in service. The best that one can hope for really is a guide to the selection of materials for field trials. But I venture to think that you could obtain a very good guide from the relative drop in fatigue value of the materials, first in air, and then in a corrosive environment approximating as closely as possible to that in the field.

Incidentally, the K-Monel itself has a particularly good endurance figure in corrosive conditions, as a generalization. In other words, the ratio of corrosive endurance to air endurance is high. From memory I think the air endurance figure is around 15 to 20 tons per square inch.

MR W. M. CATCHPOLE : It is mentioned in the paper that in lubricating oil plants using phenol extraction, 18/8 tubes have to be used in the heaters of the phenol recovery section. In extractive distillation the temperatures existing in the extraction column may be nearly 500° F, which is the temperature at which the phenol is said to become corrosive. There is one difference as compared with lubricating oil treatment, where the phenol may contain added water, in extractive distillation the phenol will be essentially anhydrous. Have you any information on the destructive nature of phenol in these conditions?

MR BURLING-SMITH : Without having looked into the matter I should imagine that the corrosive effect would be much reduced; but I cannot give you positive information on that at this juncture. You are thinking of the possibility of not using stainless steel?

MR CATCHPOLE : I was wondering if mild steel were good enough at temperatures up to 500° F in the absence of water.

MR BURLING-SMITH : I would like to look into that.

The corrosive effect of anhydrous phenol at elevated temperature on mild steel is too severe to warrant its use in this application. On the basis of plant corrosion test data on record, I would certainly recommend the selection of the 18/8 stainless steels for this elevated temperature service.

Some comparative corrosion test data for wet and dry tar vapours at the boiling point are given in the paper " Corrosion of Metals by Phenols," by T. H. Rhodes, P. A. Tiedel, and V. K. Hendricks (*Industr. Engng Chem.*, 1934, 533–34).

Dry Vapours of Tar Acids.

Metal.	Loss in weight, Mg per sq. dm. per 24 hr. Phenol.	*o*-Cresol.	*m*-Cresol.
High carbon steel	5·5	7·25	18·1
Low carbon steel	6·0	6·23	16·5
High chromium steel	1·03	2·54	3·4
Chromium–nickel steel	0·05	0·99	3·26

Wet Vapours of Tar Acids.

High carbon steel	47·2	10·9	62·8
Low carbon steel	37·2	7·2	28·3
High chromium steel	0·80	2·15	0·73
Chromium–nickel steel	1·30	1·37	0·74

MR G. F. HAZZARD : Have you any information on alloy linings which will withstand alternating alkaline-acid conditions? I am thinking particularly of a process such as the recovery of naphthenic acids, where you have three possibilities—free caustic soda, free dilute mineral acid, and free organic acid at the various phases of the process.

MR BURLING-SMITH : At what sort of temperatures?

MR HAZZARD : Not exceeding 100° C.

MR BURLING-SMITH : I should think the molybdenum-bearing stainless steel would be invaluable. It withstands the naphthenic acids and it might withstand mineral acids. How dilute are they?

MR HAZZARD : In the process organic acids are released from sodium compounds with sulphuric acid, and they should only just pass over to the acid stage. But there is always the possibility of an operator overdoing it.

MR BURLING-SMITH : It will withstand the caustic soda and the naphthenic and dilute mineral acids. Monel and Inconel are also possibilities and I would recommend corrosion tests under service conditions to assess the material best suited to your practice.

MR W. M. CATCHPOLE : One corrosion problem which, I think, has not been mentioned in the paper is that due to vanadium–nickel compounds when dealing with crude oil.

MR BURLING-SMITH : The author mentions that just at the end, I think.

MR CATCHPOLE : I did not get so far as that. But the corrosion I have mentioned is a known problem in furnaces running at high temperatures, where vanadium compounds may be deposited, particularly on tube hangers. I wonder also whether any information is available as to the lowest temperature at which vanadium and/or nickel compounds attack mild steel.

MR BURLING-SMITH : That is definitely a poser. Quite honestly I am a little vague, because surely you would not be using mild steel in an atmosphere which would give you the vanadium oxides from the oil. I understand that it is the vanadium oxide in the ash which constitutes the big problem.

MR CATCHPOLE : Yes.

MR BURLING-SMITH : The theory put forward to-day, from work that has been done, is that the vanadium oxide fluxes the protective oxide skin on the heat-resisting steel and gives a very fluid slag which is itself corrosive to the heat-resisting material. But I am in a little difficulty in visualizing the type of application you have in mind. From where would your vanadium oxide come ?

MR CATCHPOLE : I think you have really answered the question. I do not think anybody is really sure in what form the vanadium is present in crude oil and whether it can be corrosive on the inside of the equipment.

MR BURLING-SMITH : I have not heard of such a case; it has always been associated with the ash formed by burning high-vanadium oil. Perhaps, however, I should add that there is some doubt about vanadium being the only culprit. One school of thought attributes the trouble to caustic ash, which is also present in the oil.

Vote of Thanks.

THE CHAIRMAN : It only remains for me to thank Mr Morton on your behalf for having presented this paper to the Institute; as has been said, it will be very valuable indeed for reference. We are also particularly indebted to Mr Burling-Smith for having presented the paper to the meeting and for the very adequate manner in which he has replied to the discussion.

I invite you to show your appreciation.

The vote of thanks was carried with enthusiasm and Mr Burling-Smith briefly expressed appreciation.

MR B. B. MORTON, replying in writing, said : In making this closure, I would like to express my appreciation for the presentation of the paper by Mr Burling-Smith and to compliment him upon the able handling of the various questions which have risen in the discussions.

I note that Prof F. H. Garner touches upon the economics of retirement of equipment. The desire to obtain from the equipment a satisfactory life without putting into it more money than is absolutely necessary to obtain that life outlines a problem confronting the refinery engineers. The

solution of this problem is found along several lines and apparently fits into the individual thinking and peculiar conditions of each refinery. Unfortunately, the art of combating corrosion has not grown into an exact enough science to permit too good an evaluation of the life of equipment, so that in many cases the equipment is over-protected for its normal life. To offset this, many refineries prefer to counteract corrosion by applying resisting materials at only those spots where the indications are that the economic life will not be met with the initial equipment.

Dr F. Morton raises the questions concerning the detection of corrosion (*a*) in situ, and (*b*) from the deposits. He also calls attention to the difficulty of determining the line at which the composition of the lining material would change. These questions have been well answered by Mr Burling-Smith. I would like to add, however, that at the present time there are being developed instruments that determine the wall thickness of tubes and vessels even during operation, through sonic effects or by reflection of radio-active emanations. These instruments have interesting possibilities. In connexion with the question as to where the two linings merge, it was attempted to point out in the paper that this question offers its difficulties, and insofar as the writer knows, the trial and error method is the only one available. Fortunately the line of demarcation is not sharp and usually either alloy will operate within the borderline of the region where the other operates more successfully.

The questions raised by Mr E. Thornton, I believe, are adequately covered by the answers provided by Mr. Burling-Smith. I do not have at hand many histories of the exact life obtained from liners although we would like to have more data on this subject. While considerable confidence is felt in linings, especially those applied to the steel prior to the fabrication of the vessel, it will probably be some time before a satisfactory history of the performance of liners can be put together.

Dr R. F. Goldstein's interesting questions are well covered by the remarks by Mr Burling-Smith and I feel I have nothing to add on the subject of the behaviour of linings. In the matter of the carbonyl deposit, I must report that we were rather surprised at its presence and could only guess that the carbonyl formed when the unit was coming off the line or going on. The carbonyl apparently decomposed at operating temperatures. The solution in the particular case referred to was to go to nickel-free alloys such as the 28 per cent chromium one. As Mr Burling-Smith points out, the nickel-free alloys are decidedly inferior in strength and load carrying ability to the nickel-containing ones and offer a number of difficulties in their fabrication. Apparently the carbonyl formation can take place only under what must be ideal conditions.

Since some hydrogen furnace tubes after several years of service at about 1800° F have failed to show the formation of carbonyl, it may be that the excess steam used, approximately 300 to 500 per cent, may have suppressed the reaction entirely. The whole matter of the formation of carbonyl from nickel alloys is being studied in view of the Fischer–Tropsch process in the U.S.A. and some information should be forthcoming.

I am very interested in Mr Catchpole's comment on the absence of destruction of their condenser tubes in the presence of a controlled amount of ammonia. The writer should not have used the word "invariably"

since to do so invariably results in someone pointing out that the practice is quite feasible. The writer is pleased to hear Mr Catchpole's experience and has no doubt that similar experience will be recorded in the U.S.A. as soon as this paper is released. In the matter of the aqueous caustic soda solution, the writer would be inclined to suggest to Mr Catchpole the use of Type 3 Ni-Resist (Table XVII) for the impeller to handle the solution.

Mr John Henry raises an interesting subject in the matter of corrosion fatigue tests of sucker rods materials. The American Petroleum Institute has a tentative standard covering this method of testing and considerable work is being done in the U.S.A. to further improve the test. Dr B. B. Wescott, of the Gulf Research and Development Co., is probably the highest authority on this subject in the U.S.A. and I am sure he would be glad to discuss the various features of the test if Mr Henry would care to take them up with him. While these tests as outlined by the American Petroleum Institute specifications are useful in segregating a steel from a group of steels, the writer is rather inclined to question the correlation between these tests and actual performance in a well presumably represented by one of the three standard tests: non-corrosive (air); brine corrosive; and sulphide brine corrosive conditions. The air endurance limit value of K Monel in the same condition of heat treatment applying to the sucker rods referred to in the paper is 44,000 to 58,000 p.s.i. We have for some time been trying to have corrosion fatigue tests made on K Monel, but the equipment on which we would like to have the tests made has been tied up on other equally as important work. Since these rods have given excellent service in a very corrosive well, it would be interesting to see what the results from the corrosion fatigue tests are and how they tie in with the known performance of the rod.

Mr Catchpole raises another question, namely, concerning the corrosion of phenolic waters. We are, at the present time, ascertaining the corrosiveness of phenols in the presence of organic materials and hope to have some information in the very near future. I feel that Mr Burling-Smith has competently dealt with the points raised here and only offer the above in the thought that the data may be of interest at some later date.

In connexion with the inquiry by Mr G. F. Hazzard concerning an alloy lining to resist alternating alkaline-acid conditions, I concur with Mr Burling-Smith in his suggestion of the molybdenum-bearing stainless steel. I also feel that Monel or Inconel would be satisfactory, but here again would like to consult with Mr Burling-Smith in suggesting a corrosion test.

Mr Catchpole raises the interesting questions associated with the behaviour of the vanadium compounds upon the heat-resisting alloys. This problem is receiving considerable attention in view of the hopes that the cheaper, bottom cuts of petroleum can be used in the gas turbines. The danger here is that the vanadium oxide liberated from the bottoms destroys the blades. We are actively investigating the behaviour of different heat resisting materials in the presence of vanadium oxides, but so far have no answers to what would be satisfactory. I agree with Mr Burling-Smith that one would have to be as careful of caustic ash as of the vanadium. In this connexion the results from the turbine that is projected to burn powdered coal is awaited with interest since there is some thought that possibly here the caustic constituents may be active in injuring the blading.